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The Third Law of Thermodynamics: Phase equilibria and phase diagrams at low temperatures

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ARTICLE INFO

Article history:

Received 11 August 2017
 Received in revised form
 10 November 2017
 Accepted 19 November 2017
 Available online 1 December 2017

Keywords:

Third Law of Thermodynamics
 Phase equilibria
 Low temperature phase equilibria
 Nernst-Planck-Simon statement

ABSTRACT

Great progress has been made over the recent decades in the application of computational thermodynamics (Calphad) and theoretical methodologies (CVM) including so-called first principles approaches to modeling thermodynamic properties and the calculation of phase diagrams of materials. The aim of this paper is to call attention to considerations of the THIRD LAW OF THERMODYNAMICS when evaluating these results when applied to low temperature phase equilibria. In this effort we call attention to the essential content of the modern version of this third principle of thermodynamics using an historical and pedagogical approach. An appreciation of the constraints of the THIRD LAW is shown to be valuable in projecting possible low temperature phase fields and boundaries and predicting thermodynamically consistent phase diagram configurations as $T \rightarrow 0$ K. The ideas of Simon regarding aspects or subsystems are shown to be of paramount importance in assessing the thermodynamic properties of materials at low temperatures.

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1. Introduction

In view of the great progress made over the past two decades or so in computational thermodynamics and the calculation of phase diagrams [1,2] it is rather remarkable that the results very seldom have been scrutinized in terms of the demands of the **THIRD LAW OF THERMODYNAMICS**. The cluster variation method (CVM) [3–6] has emerged as the most powerful method for modeling the configurational energetics of alloys and predicting binary and ternary phase equilibria and associated phase diagram configurations. However, even in this methodology considerations of the Third Law are generally ignored when compiling and evaluating the soundness of the results. Furthermore, it should be pointed out that Third Law considerations can be very valuable in assessing possible alternative phase diagram topologies and phase boundaries based on projections to low temperatures [7,8]. However, there is a glaring paucity of discussion regarding the implications and restrictions of the Third Law related to phase equilibria at low temperatures and this situation often appears to derive from a lack of a full understanding of the modern rigorous statement of the Third

Law of Thermodynamics and its scope as it applies to heterogeneous phase equilibria. It is the purpose of this paper to elucidate the content of a comprehensive version of the Third Law and to illustrate its importance in various selected contexts of particular interest to phase transformation behavior in materials science. We begin the discussion with a brief history of the evolution of the Third Law arriving at the Nernst-Planck-Simon statement of this fundamental principle.

2. Historical perspective

The Third Law of Thermodynamics was born in chemistry, in particular, in the nascent field of physical chemistry just after 1900 some 25 years or so after the treatise of Gibbs [9]. It emerged as the Nernst Heat Theorem in 1906 [10,11] during a period of intense discussion of chemical equilibrium constants and the possibility of calculating equilibrium constants for a reaction as a function of temperature solely from thermal data. The problem was essentially embodied in solving the so-called Gibbs-Helmholtz equation:

$$\Delta G = \Delta H + T \frac{\partial \Delta G}{\partial T} \quad (1a)$$

or

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$$\Delta G(T) = \Delta H(T_1) + \int_{T_1}^T \Delta C_p dT - T \left[\int_0^T \frac{\Delta C_p}{T} dT + \Delta S_0 \right] \quad (1b)$$

which could not be determined by thermometric methods because the integration constant ΔS_0 , is the change in entropy for the reaction at 0 K which was inaccessible. T. Richards [12] at Harvard around 1900 had compiled a plethora of ΔH and ΔG versus temperature data determined calorimetrically and galvanically whilst his Ph.D. student G. Lewis analyzed Equation (1a) and (1b) in his Ph.D. thesis work. (Ironically, Lewis was never made privy to this array of data [12]). Walter Hermann Nernst in Germany upon examining the data noted the asymptotical behavior of the ΔH and ΔG curves as $T \rightarrow 0$ K. In particular, he asserted that $\frac{d\Delta H}{dT} \rightarrow 0$ and $\frac{d\Delta G}{dT} \rightarrow 0$ as $T \rightarrow 0$ and thus $\Delta S_0 = 0$.

Now, in principle, thermometric measurements alone could be used to calculate chemical equilibria over temperature ranges where accurate thermal data could be accessed. This is the seminal form of the Nernst Heat Theorem which would be the basis for a Third Law of Thermodynamics. The Heat Theorem was highly controversial from the onset of its appearance with doubts expressed as to its generality and significance with commentary coming from luminaries such as Einstein and others. However, Planck [13] in the third edition of his Treatise on Thermodynamics published in 1910 cited the Nernst Heat Theorem as of fundamental importance in the development of thermal physics and chemistry and subsequently promulgated and extended the principle. Based on a quantum and a statistical mechanics perspective Planck asserted that the absolute entropy of chemically homogeneous substances at $T = 0$ K is identically equal to zero ($S_0 = 0$) independent of the pressure, state of aggregation or special chemical modification in a state of thermodynamic equilibrium. From a statistical mechanics viewpoint this indicates that since the absolute entropy of a substance is given by $S = k_B \ln \Omega$ where Ω is the thermodynamic probability or number of distinguishable quantum states or microstates compatible with the macroscopic thermodynamic state, at $T = 0$ K the ground state entropy is given by $S_0 = k_B \ln g_0$ where g_0 is the degeneracy of the ground state indicating that $g_0 = 1$ (the ground state is non degenerate) and $S_0 = 0$. It should be noted that this is true of ideal Fermion and Boson gases as shown in quantum statistical mechanics (Fermi-Dirac and Bose-Einstein statistics). Furthermore, it must be pointed out that the original Heat Theorem when applied to a simple chemical reaction $A + B \rightarrow AB$ indicating $\Delta S_0 = S_0^{AB} - S_0^A - S_0^B = 0$ at $T = 0$ K, only indicates that the absolute entropies of the reactants and products reach a constant value (per atom) at 0 K. Importantly the vanishing of the entropies, S_0^{AB} , S_0^A and S_0^B at absolute zero (that is, $S_0^{AB} = S_0^A = S_0^B = 0$) is consistent with the Nernst Heat Theorem.

Sir Francis Simon (1893–1956) a former student of Nernst promoted the importance of the Heat Theorem as a Third Law of Thermodynamics over many years in an expanded form asserting that $S_0 = 0$ for all thermodynamic systems or subsystems in internal equilibrium [11,14,15]. Simon referred to the subsystems as aspects of a composite thermodynamic system comprised of the vibrational modes of the crystal lattice, the free electron gas of a metallic solid, spin systems (electronic and nuclear), configurational and structural variants as well as isotope mixtures. According to Simon the Third Law is applicable individually to each aspect or subsystem of the total composite thermodynamic system provided the subsystem is in thermodynamic equilibrium. This strong statement of the Third Law is the **Nernst-Planck-Simon** version which is stated formally as follows:

The THIRD LAW OF THERMODYNAMICS establishes a

fundamental lower limit for the temperature of matter called Absolute Zero (0 K) and the natural origin from which to measure/calculate the absolute entropy of a substance. THE ENTROPY OF ALL SUBSTANCES IN INTERNAL THERMODYNAMIC EQUILIBRIUM AT $T = 0$ K IS ZERO, THAT IS, $S_0 = 0$ INDEPENDENT OF PRESSURE, EXTERNAL FIELDS OR STATE OF AGGREGATION. The THIRD LAW can be applied individually to various aspects or subsystems of the material e.g. spin systems, vibrational and rotational states, etc. provided they are in thermodynamic equilibrium.

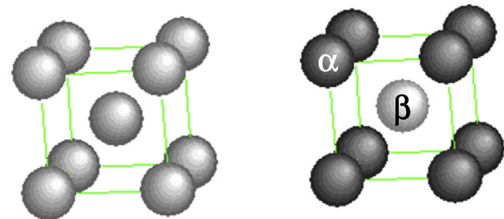
It follows from this statement of the THIRD LAW that ΔC_p and $C_p \rightarrow 0$ as $T \rightarrow 0$ K and that the coefficient of thermal expansion of a substance $\alpha \rightarrow 0$ as $T \rightarrow 0$ K. Furthermore, it is readily demonstrated that this version of the THIRD LAW is consistent with the notion of the unattainability of 0 K in a finite number of cyclic steps [15].

2.1. Phase separation and ordering: A2 \rightarrow B2

Let us begin our discourse by looking at the well-known A2 \rightarrow B2 ordering transition in binary alloys within the context of Third Law considerations employing the so-called generalized Bragg-Williams approximation wherein we include first and second-nearest neighbor pairwise interactions in formulating the solution energetics. Our approach essentially follows that of Ino [16] in his treatment of decomposition and ordering in bcc binary alloys. Before proceeding the reader is reminded of a few salient points regarding this mean field approach to central issues regarding its application. In referring to a Bragg-Williams model [17] applied to ordering in alloys, it should be pointed out that the original Bragg-Williams approach did not describe the energetics of an A-B binary alloy generally in terms of short-range forces associated with pairwise interactions or A-A, B-B and A-B bonds typically employed in quasichemical models. The energetics of the solution was formulated in terms of an “interchange energy”, W , associated with moving A and B atoms from “right” positions to “wrong” positions in the superstructure and the energy W is proportional to the degree of **long range order** (η) defined in terms of the occupancies of relevant sublattices α , β , γ , etc. defining the evolving superlattice. For the B2 or ordered phase described by α and β sublattices (See Fig. 1). The long range order (LRO) parameter is written generally as:

$$\eta = \frac{(r_\alpha - X_A)}{Y_\beta} = \frac{(r_\beta - X_B)}{Y_\alpha} \quad (2)$$

- Where: r_α is the fraction of specified α -sites occupied by A atoms (“right” atoms)



A2 Disordered Structure

B2 Ordered Structure

Fig. 1. Disordered (A2) and ordered (B2) phases showing α and β sublattices of the B2 superstructure.

- r_β is the fraction of specified β -sites occupied by B atoms (“right” sites)
- Y_α and Y_β are the fraction of α -sites and β -sites in the ordered superstructure with X_A and X_B the atomic fractions of species A and B

(Note: For the ordered B2 structure the order parameter η can be written as $\eta = \frac{R-W}{R+W}$ where R is the total number of atoms in the “right” positions and W is the total number atoms in “wrong” positions giving $\eta = 1$ for the perfectly ordered structure). Importantly, the classic Bragg-Williams approach wherein it is assumed that the interchange parameter is given by $W = \eta W_0$ (where W_0 is the value of W in the perfectly ordered state) makes no explicit use of a detailed incorporation of short-range forces as mentioned above and implicitly assumes that the mixing on the sublattices is random (regular solution).

Random mixing on the sublattices renders this a mean field theory essentially equivalent to the Weiss molecular field theory in the underlying physics and thus neglects local correlations. More rigorous treatments such as the Bethe pair approximation [18,19] and the cluster variation method (CVM) [3–6] provide a markedly improved calculation of the entropy and local correlations using atomic clusters such as pairs or tetrahedra rather than individual atoms immersed in a mean field. The quasichemical approach of Bethe was the precursor of the CVM methodologies [20]. These local correlations are of paramount importance at high temperatures relative to the critical temperature T_C of the ordering reaction but become less important at lower temperatures where the so-called “point cluster” mean field approximation of a generalized Bragg-Williams model (which is homologous with the zeroth approximation of the quasichemical schemes invoking A-A, B-B and A-B pairwise bond energies) is a good approximation.

Thus, we examine the A2 \rightarrow B2 transition using 1st and 2nd nearest – neighbor interactions as mentioned above and write the free energy of mixing $F_m(c, \eta)$ of the binary A-B alloy as a function of concentration c and LRO order parameter η as follows:

$$F_m(c, \eta) = Nc(1-c)(8V + 6U) + \frac{N\eta^2}{4}(8V - 6U) + \text{entropic terms} \quad (3)$$

where $C_\alpha = c - \frac{\eta}{2}$ and $C_\beta = c + \frac{\eta}{2}$ are the fraction of α and β sublattice sites occupied by B atoms, respectively; η is the order parameter defined above and N is the total number of atoms of the solution. The interchange parameters V and U characterizing the atomic interactions for the 1st and 2nd nearest-neighbor shells are defined as:

$$1^{\text{st}} \text{ nn: } V = \frac{1}{2} [E_{AA}^{(1)} + E_{BB}^{(1)} - 2E_{AB}^{(1)}] \quad (4a)$$

$$2^{\text{nd}} \text{ nn: } U = \frac{1}{2} [E_{AA}^{(2)} + E_{BB}^{(2)} - 2E_{AB}^{(2)}] \quad (4b)$$

with $E_{AA}^{(i)}$, $E_{BB}^{(i)}$ and $E_{AB}^{(i)}$ taken as the effective strengths of the 1st nn ($i = 1$) and 2nd nn ($i = 2$) AA, BB and AB atomic bonds or interaction energies. In this convention, $V < 0$ is the case for the B2 superstructure. (It should be noted that the interchange energy in the original Bragg – Williams treatment $W_0 = -2z_1V$ with $z_1 = 8$, the coordination of the 1st nn shell, leading to $T_C = -4V/k_B$). The heat of mixing of the random solid solution relative to the pure components A and B in our generalized Bragg-Williams model is $\Delta H_m = Nc(1-c)(8V + 6U)$ incorporating the higher interactions in the 2nd nn shell ($z_2 = 6$).

The entropic terms deriving from the assumption of random

mixing on the α and β sublattices are given by:

$$-TS_m = \frac{Nk_B T}{2} \left(\begin{aligned} & \left((1-c+\frac{\eta}{2}) \ln(1-c+\frac{\eta}{2}) + (c-\frac{\eta}{2}) \ln(c-\frac{\eta}{2}) \right) \\ & + \left((1-c-\frac{\eta}{2}) \ln(1-c-\frac{\eta}{2}) + (c+\frac{\eta}{2}) \ln(c+\frac{\eta}{2}) \right) \end{aligned} \right) \quad (5)$$

in this approximation. As mentioned above, this description of the configurational entropy (we are ignoring other possible entropic contributions such as vibrational modes) is not accurate at temperatures high relative to the critical temperature but becomes a reasonable approximation at lower temperatures.

Setting $\frac{\partial F_m}{\partial \eta} = F_\eta = 0$ and $F_{\eta\eta} = 0$ allows one to calculate a locus of critical points ($\eta = 0$) as a function of concentration and temperature given by:

$$\frac{T_C(c)}{T_C(c=0.5)} = 4c(1-c) \quad (6)$$

where $T_C(c=0.5) = \frac{(3U-4V)}{k_B}$ is the critical temperature for ordering at the equiatomic composition $c = 0.5$. When $U = 0$ the associated free energy vs. composition curve is concave upwards ($F_{cc} > 0$) for all temperatures $T > 0$ K (See Fig. 2b) becoming linear at $T = 0$ K as shown below. The ordering at the transition temperature marks the onset of a second order phase transformation according to Ehrenfest [21] in this approximation at all compositions exhibiting the well-known textbook behavior shown in Fig. 3a–b. The singularity

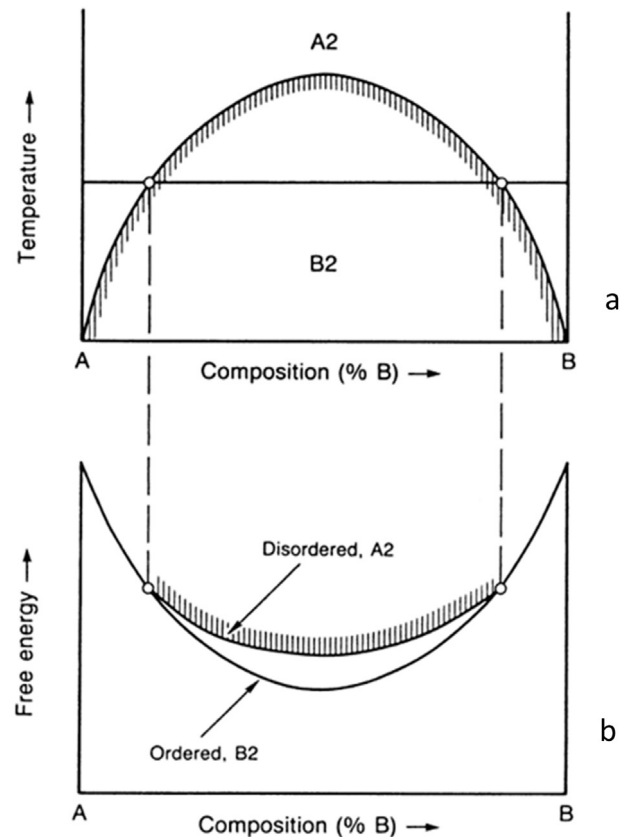


Fig. 2. Phase diagram showing disorder \rightarrow order line of critical points and associated free energy – composition curves. The cross-hatched loci indicate the second order/higher order nature of the phase transition. Note: this diagram is not consistent with the Third law as discussed in the text.

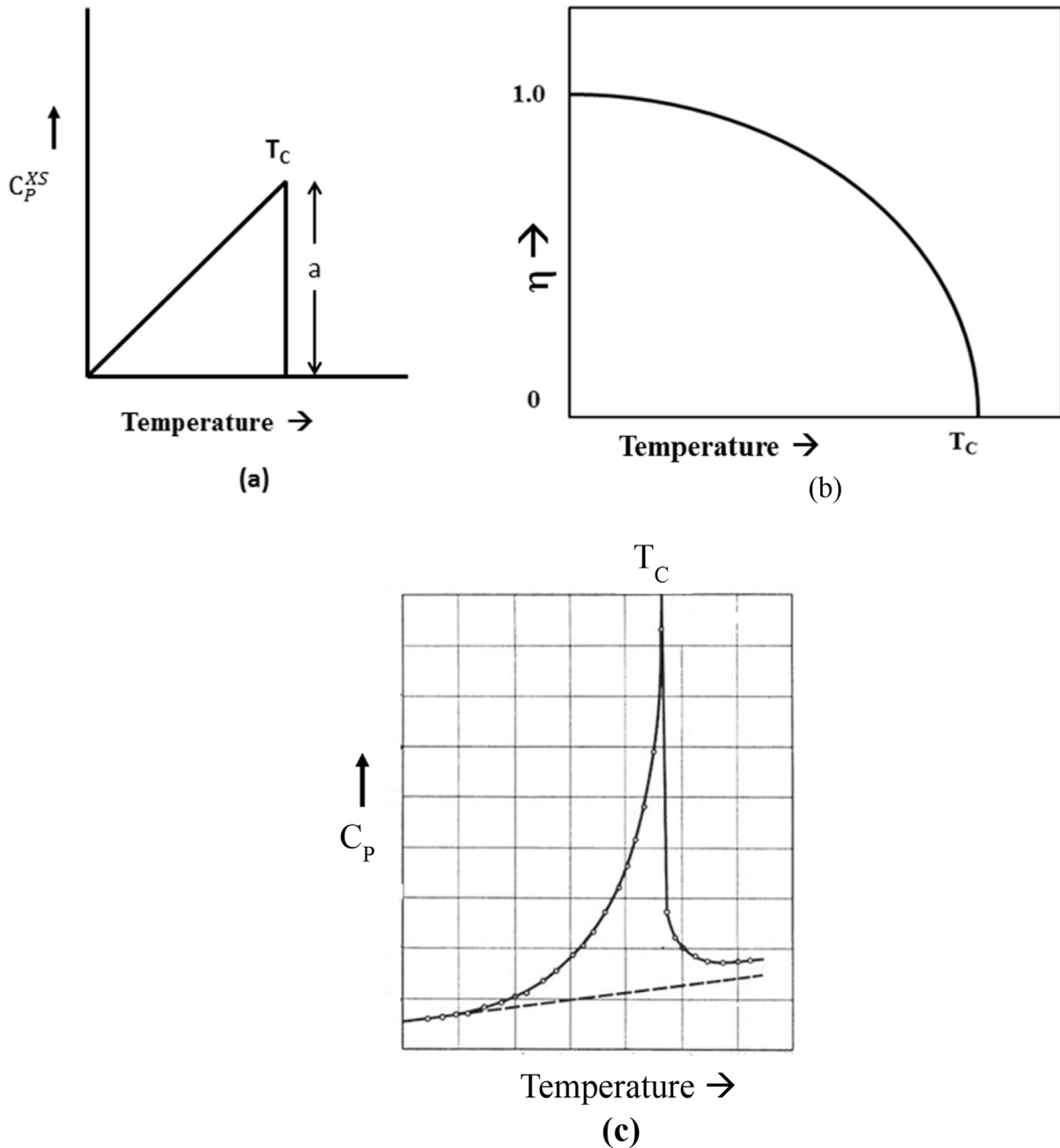


Fig. 3. a) Variation of the excess heat capacity versus temperature for a second order transition such as A2 → B2 predicted by the Bragg-Williams approximation. b) Variation of the long range order (LRO) parameter η versus temperature for a second order transition according to the Bragg-Williams model. c) Typical experimental results showing the variation of the heat capacity with temperature for a higher order or so-called λ transition. (Note the curve looks like the Greek letter lambda.)

in the heat capacity according to this Bragg-Williams model is a finite discontinuity compared to the experimental result such as in β -brass as depicted in Fig. 3c indicative of a so-called higher order λ -transition. Most importantly in this discourse, if one cools any alloy composition $c < 0.5$ from the disordered region of the phase diagram to $T = 0$ K under equilibrium conditions the resulting imperfectly ordered state $\eta = 2c$ will have a residual configurational entropy in violation of the Third Law of Thermodynamics. However, if the solution energetics include the 2nd nn interactions, that is, $U > 0$ and the optimized order parameter ($F_\eta = 0$) at any value of composition and temperature given by the transcendental relation:

$$\frac{T}{T_C} = \frac{4\eta}{\ln\left(\frac{(1-c+\frac{\eta}{2})(c+\frac{\eta}{2})}{(1-c-\frac{\eta}{2})(c-\frac{\eta}{2})}\right)} \quad (7)$$

is inserted into Equation (3) giving $F(c,\eta)_{\min}$, free energy vs. composition curves can be constructed which produce markedly different results. These free energy curves exhibit inflection points ($F_{cc} = 0$) and local minima indicative of phase separation in conjunction with the ordering reaction. See Fig. 4a–b. Most importantly, the equilibrium state at $T = 0$ K for $0 < c < 0.5$ is a two-phase mixture consisting of pure A and perfectly ordered B2 ($c = 0.5$) the relative proportions given by the familiar lever rule.

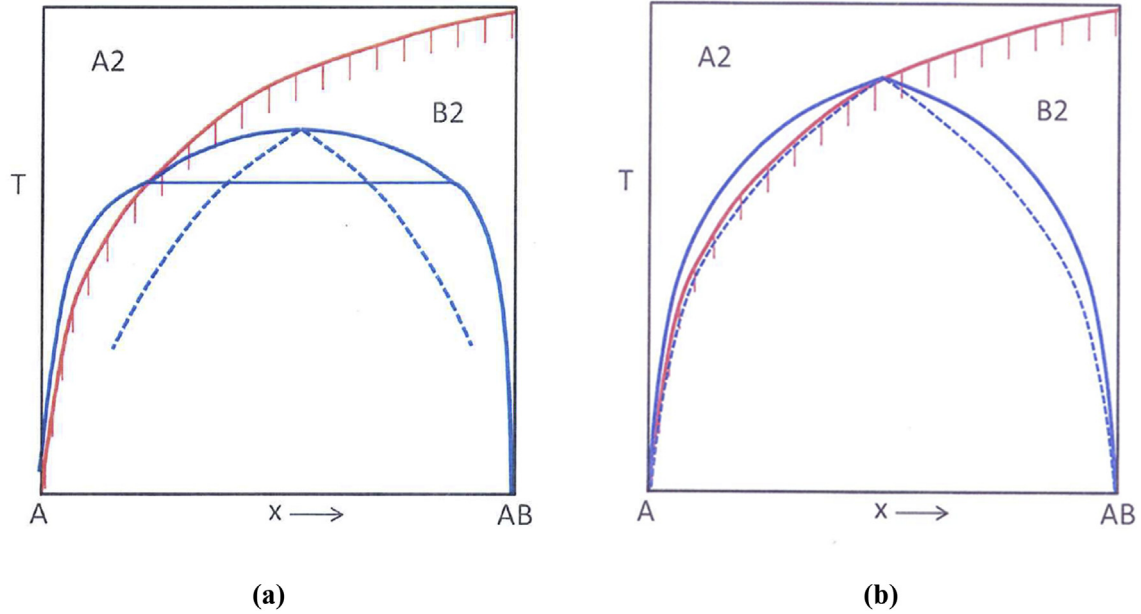


Fig. 4. Phase diagrams associated with the A2→B2 transition predicted by a generalized Bragg-Williams model taking into account 1st and 2nd nearest-neighbor interactions wherein concomitant ordering ($V < 0$) and clustering ($U > 0$) tendencies are embodied in the solution energetics. The hatched locus delineates the locus of critical points for the A2→B2 transition and the solid lines are solvi showing two-phase fields B2' + B2'' and A2 + B2. The dashed locus delineates a chemical spinodal line in the ordered B2 phase—a so-called conditional thermodynamic instability contingent on prior ordering. a) Defining the parameter $R = 3U/4|V|$ this configuration occurs for $R \sim 1/4$ or $U \sim 1/3|V|$. b) This tricritical point occurs for $R \sim 1-4$. Clearly the phase diagrams essentially show the intersection of the higher order disorder→ order transition with a miscibility gap leading to a synergistics of ordering and phase separation. See Ref. [16] for more details.

This is clearly in accord with the Third Law wherein the configurational entropy of this aspect of the system vanishes at $T = 0$ K. It is interesting to note that at $T = 0$ K, if $U = 0$ the free energy functional wherein $\eta = \eta_{opt} = 2c$ (η_{opt} being the optimum order parameter discussed above) becomes $F = 8NcV$ for an imperfectly ordered solid solution and equal to $4NV$ at the stoichiometric composition $c = 0.5$. These off-stoichiometric imperfectly ordered single phase solutions have residual entropy as cited above but it should be noted that this linear free energy functional is degenerate; the free energy with $U = 0$ is the same as that of a two-phase mixture of A2 + B2 governed by the lever rule. Furthermore, the second derivative F_{cc} is obviously zero across the entire composition range. However, if $U > 0$, the free energy at 0 K becomes $F = Nc(8V + 6U) - 12NUc^2$ and $F_{cc} = -24NU$. The degeneracy is removed rendering all solutions in the range $0 < c < 0.5$ thermodynamically unstable with respect to phase separation into the zero entropy state of the A2 + B2 phase mixture. See Fig. 5. It should be pointed out that Kubo and Wayman [22] using the static concentration wave (SCW) methodology of Khachatryan [23] with 1st and 2nd nearest-neighbor pairwise interactions which incorporates Fourier transform techniques within the Bragg-Williams model to express the free energy arrived essentially at the same results as Ino [16] as cited and extended above as well as calling attention to accordance with the Third Law of Thermodynamics.

Another important issue related to A2→B2 ordering behavior and the THIRD Law is the variation of the order parameter η with temperature $\frac{\partial \eta}{\partial T}$ as $T \rightarrow 0$. At any composition we can write $dE = TdS + H'd\eta$ and $dF = -SdT - \eta dH'$, where H' is a quasi-thermodynamic conjugate field related to a difference in chemical potential between sublattices. Using a standard Maxwell relation applied to these relations leads to $\frac{\partial \eta}{\partial T} \rightarrow 0$ as $T \rightarrow 0$ since $\frac{\partial S}{\partial T} \rightarrow 0$ as $T \rightarrow 0$ according to the THIRD LAW. We arrive at this conclusion solely based on classical thermodynamics without invoking quantum theory.

It is interesting to compare this result to that deriving from the

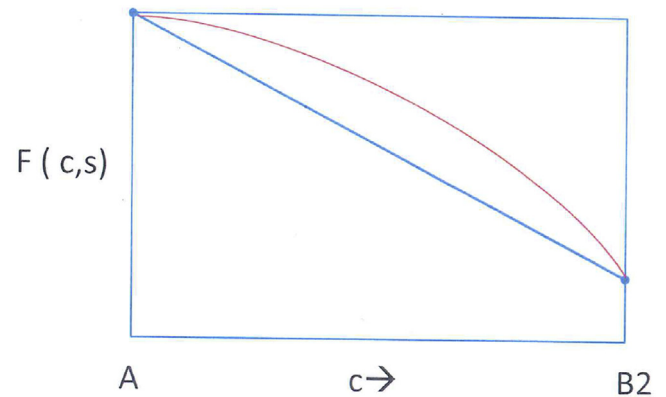


Fig. 5. Free energy versus composition at $T = 0$ K for A2→B2 ordering. The linear plot is for 1st nn interactions only whereas the parabolic curve is when 2nd nearest-neighbor interactions are included in the solution energetics. When $U \neq 0$ all solutions are thermodynamically unstable with respect to phase separation into pure A and B2 with zero entropy.

Landau theory of the second order transitions [24]. Using the usual truncated Landau expansion for the excess free energy $G(\eta) - G(0) = A\eta^2 + B\eta^4 \dots$ with $A = a(T-T_c)$ and $a > 0$, yields for the variation of the degree of order with temperature at the stoichiometric composition B2 $\eta = \left(\frac{T_c - T}{T_c}\right)^{\frac{1}{2}}$ leading to $\frac{\partial \eta}{\partial T} = -\frac{1}{2T_c}$ at $T = 0$ K which clearly is not in accord with the THIRD LAW. Presumably, higher order terms could bring the Landau theory in line with the thermodynamics discussed above.

The Bragg-Williams model readily allows the determination of $\frac{\partial \eta}{\partial T}$ as a function temperature and composition showing η going to $2c$ as $T \rightarrow 0$ K and $\frac{\partial \eta}{\partial T} \rightarrow 0$ as $T \rightarrow 0$ K. In both the Bragg-Williams and Landau descriptions the excess heat capacity of the ordering aspect of the system $\Delta C_p \rightarrow 0$ as $T \rightarrow 0$ K [15]. See Fig. 3a.

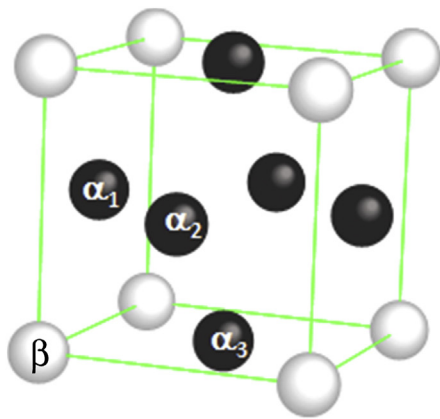
2.2. Phase separation and ordering: A1 → L1₂

Let us now apply the generalized Bragg-Williams approach to the A1(fcc) → L1₂ (A₃B) first-order transition as shown in Fig. 6a–c wherein four sublattices (three of which are crystallographically equivalent) are used to describe the L1₂ superstructure [25]. The free energy of mixing $F_m = F(c, \eta)$ for this case can be written as:

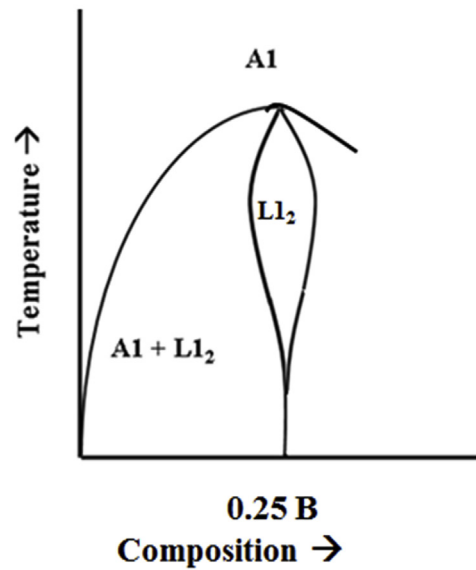
$$F(c, \eta) = Nc(1 - c)[12V + 6U] - \frac{3N\eta^2 [-4V + 6U]}{16} + \text{Entropic Terms} \quad (8)$$

where the entropic terms expanded as $-TS_m$ are given by:

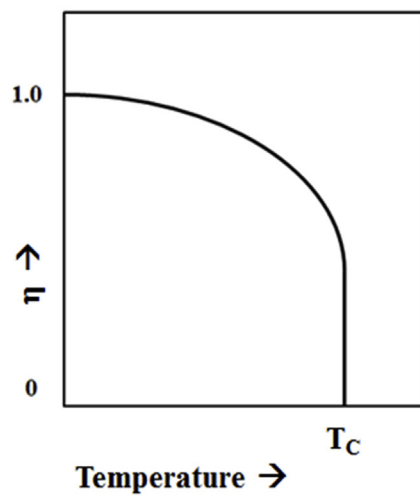
$$-TS_m = \frac{Nk_B T}{4} \left(3\left(c - \frac{\eta}{4}\right) \ln\left(c - \frac{\eta}{4}\right) + 3\left(1 - c + \frac{\eta}{4}\right) \ln\left(1 - c + \frac{\eta}{4}\right) + \left(c + \frac{3\eta}{4}\right) \ln\left(c + \frac{3\eta}{4}\right) + \left(1 - c - \frac{3\eta}{4}\right) \ln\left(1 - c - \frac{3\eta}{4}\right) \right) \quad (9)$$



(a)



(b)



(c)

Fig. 6. a) L1₂ superstructure showing four conventional sublattices. b) Section of A-B binary diagram showing A₃B (L1₂) ordered phase bounded by two-phase regions because the A1 → L1₂ disorder–order transition is first order. c) Variation of the (LRO) order parameter η , with temperature for the first order A1 → L1₂ phase change according to Bragg-Williams approximation.

Taking $\frac{\partial F}{\partial \eta} = 0$ gives the variation of the order parameter η at equilibrium as a function of temperature and composition expressed in the transcendental equation:

$$\ln \frac{\left(c + \frac{3\eta}{4}\right)\left(1 - c + \frac{\eta}{4}\right)}{\left(c - \frac{\eta}{4}\right)\left(1 - c - \frac{3\eta}{4}\right)} = \frac{4(2V - 3U)\eta}{k_B T} \quad (10)$$

which can be solved graphically or numerically. The typical variation of η with temperature for the first order transition is depicted in Fig. 6c. Substituting the optimum or equilibrium value of η into Equation (8) allows one to calculate free energy vs. composition curves as a function of temperature as shown in Fig. 7. When only the 1st nearest-neighbor interactions are included ($V < 0, U = 0$) the F vs. c curves for the ordered and disordered phases generally exhibit a positive curvature whereas if $U > 0$ inflection points and regions of negative curvature emerge indicating instability with respect to phase separation in non-stoichiometric imperfectly ordered solid solutions. See Refs. [25–28] for detailed analyses of the interplay of ordering and spinodal decomposition in the formation of ordered precipitate phases in fcc alloys. Importantly, in this generalized Bragg-Williams approach to $A1 \rightarrow L1_2$ ordering at all the compositions produces a similar η vs. T behavior as shown above with $\eta_{opt} \rightarrow 4c$ as $T \rightarrow 0$ K with $d\eta/dT \rightarrow 0$ as demanded by the THIRD Law. This is again in contrast to the result of the Landau theory wherein $d\eta/dT \neq 0$ in the limit $T \rightarrow 0$ K.

Let us now examine the generalized Bragg-Williams thermodynamic behavior of the $A1 \rightarrow L1_2$ ordering as $T \rightarrow 0$ K. The free energy functional of solid solutions at 0 K is given by:

$$F(c, \eta) = Nc[12V + 6U] - Nc^2[12V + 6U] + \frac{3N\eta^2[4V - 6U]}{16} \quad (11)$$

and taking $\eta = \eta_{opt} = 4c$, this becomes:

$$F(c, \eta) = Nc[12V + 6U] - 24UNc^2 \quad (12)$$

The free energy vs. composition curve for the range $0 < c < 0.25$ exhibits a negative curvature $F_{cc} = -48NU$ indicating that all homogeneous solid solutions at $T = 0$ K are unstable with respect to phase separation into a two-phase mixture of pure A and A_3B the

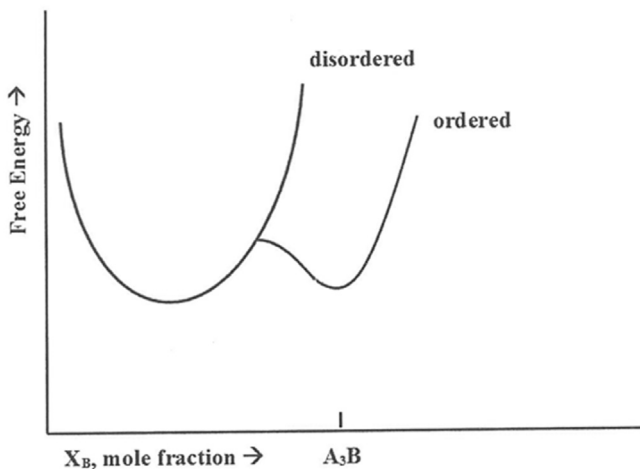


Fig. 7. Schematic free energy versus composition curves for the disordered ($A1$) and ordered $L1_2$ phases according to the generalized Bragg-Williams approach taking into account 1st and 2nd nearest-neighbor interactions. Note the appearance of a region of negative curvature for imperfectly ordered solid solutions.

relative proportions given by the lever rule and consistent with the Third Law.

However, if only 1st n-n interactions are taken into account ($U = 0$) the free energy vs. composition curve of the solid solutions (with positive entropy) is linear (zero curvature) and the same as that of a mixture of pure A and the fully ordered A_3B which has zero entropy. This degeneracy is lifted when 2nd n-n interactions ($U > 0$) are included in the free energy expression in accordance with the Third Law as shown above. See Fig. 8.

2.3. Phase separation and ordering: $A1 \rightarrow L1_0$

Let us close this portion of the discussion of solution energetics and stability related to order \rightarrow disorder transitions and the Third Law of Thermodynamics by looking at the $A1 \rightarrow L1_0$ transformation. This ordering involves a cubic \rightarrow tetragonal change of phase in contrast to the cubic \rightarrow cubic $A2 \rightarrow B2$ and $A1 \rightarrow L1_2$ systems discussed above. Nix and Shockley [29] in the late 1930s analyzed the $A1 \rightarrow L1_0$ transition and characterized the ordering reaction as second order according to the conventional Ehrenfest classification based on a rigid lattice model incorporating only 1st n-n pairwise interactions ($V < 0, U = 0$). However, Guggenheim [30] in 1952 using a quasichemical tetrahedron approximation was able to capture the first order character (1st n-n interactions only) within this precursor of later cluster variation methods (CVM). More recently, Mohri and coworkers [31–34] have studied the transition including lattice vibrations. The modern theories definitively characterize the $A1 \rightarrow L1_0$ transition as first order and have identified a so-called $L1'$ ($P4/mmm$) phase at low temperatures [35,36]. It should be noted that Larikov, Geischenko and Falchenko [37] asserted that this cubic \rightarrow tetragonal transformation is first order if changes in lattice dimensions and associated elastic strain are incorporated in the thermodynamics without correlations or many-body interactions within a modified Bragg-Williams approximation. In the following discussion leading to some interesting results related to Third Law considerations we formulate the thermodynamics of the $A1 \rightarrow L1_0$ transition employing the approach of Cheong and Laughlin [38] as elaborated in the computational study by Soffa, Laughlin and Singh [39] which includes 1st n-n and 2nd n-n interactions as well as lattice distortion and elastic relaxation in the free energy functional.

The free energy of mixing for the $L1_0$ ordering A-B alloy is first written as:

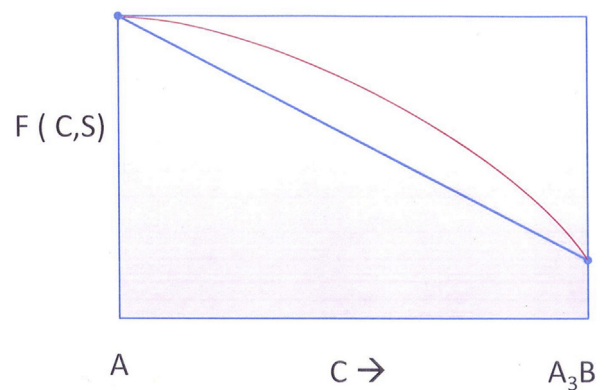


Fig. 8. Free energy versus composition diagram at $T = 0$ K for the $L1_2$ ordering system. Note that the linear curve is for $U = 0$ and the parabolic curve is for $U \neq 0$. The parabolic curve indicates that all solutions are unstable with respect to phase separation into pure A and $L1_2$ with zero residual entropy.

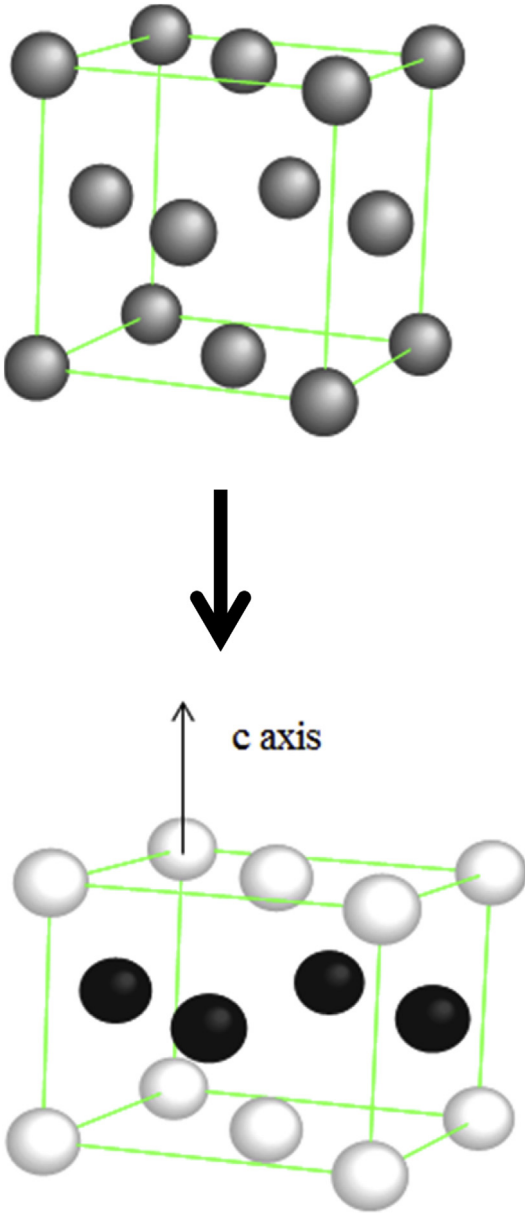


Fig. 9. A1 \rightarrow L1₀ ordering showing atomic rearrangement and elastic relaxation giving rise to cubic \rightarrow tetragonal change in symmetry.

$$F_m(c, \eta, e) = Nc(1-c)(12V + 6U) + \frac{N\eta^2}{4}(4V - 6U) + \text{entropic terms} \quad (13)$$

where the A and B atoms occupy the sites of the fcc parent lattice with the layered superstructure described in terms of two sublattices with the first coordination shell along the twelve $\langle 110 \rangle$ directions and the second along six $\langle 100 \rangle$ directions. See Fig. 9a. The entropic terms assuming random mixing on the sublattices can be written as:

$$-TS_m = \frac{Nk_B T}{2} \left(\left(c - \frac{\eta}{2} \right) \ln \left(c - \frac{\eta}{2} \right) + \left(1 - c + \frac{\eta}{2} \right) \ln \left(1 - c + \frac{\eta}{2} \right) \right. \\ \left. + \left(1 - c - \frac{\eta}{2} \right) \ln \left(1 - c - \frac{\eta}{2} \right) + \left(c + \frac{\eta}{2} \right) \ln \left(c + \frac{\eta}{2} \right) \right) \quad (14)$$

This free energy functional will lead to a second/higher order transition similar to the results of Nix and Shockley [29] in their classic analysis cited above. However, if one expands the free energy to include an elastic relaxation term related to the change in crystal structure shown in Fig. 9b we can write the modified solution energetics as:

$$F_m(c, \eta, e) = Nc(1-c)(12V + 6U) + \frac{N\eta^2}{4}(4V - 6U) - 4Nec^2\eta^2 + \text{entropic terms} \quad (15)$$

where e is a positive constant which is a function of the elastic constants and transformation strain. Adding this elastic coupling energy leads to a very different behavior, namely, the A1 \rightarrow L1₀ transition is rendered first order beyond a threshold value of a parameter $\alpha = \frac{e}{|-4V+6U|}$. At low temperatures and low concentrations the transition changes to higher order for low values of the α parameter.

Now let us look at the free energy of homogeneously ordered solutions in the range $0 < c < 0.5$ as $T \rightarrow 0$ K and $\eta \rightarrow 2c$. In the absence of the elastic term the curvature of the free energy–composition curve for imperfectly ordered states ($\eta = 2c$) is given by:

$$F_{cc}(c, \eta, e) = -8N(2V + 3U) \quad (16)$$

which is negative for $[2V + 3U] > 0$, which cannot be positive if only 1st n-n interactions are taken into account, that is when $U = 0$. However, if 2nd n-n interactions are included ($U > 0$) the curvature is negative provided $U > -\frac{2}{3}V$. If this condition doesn't hold the elastic term can contribute to the thermodynamic instability of the homogeneously ordered single phase states consistent with the THIRD LAW. Also, third and fourth n-n interactions can contribute to the instability of these ordered states [40,41]. Finally, again $d\eta/dT$

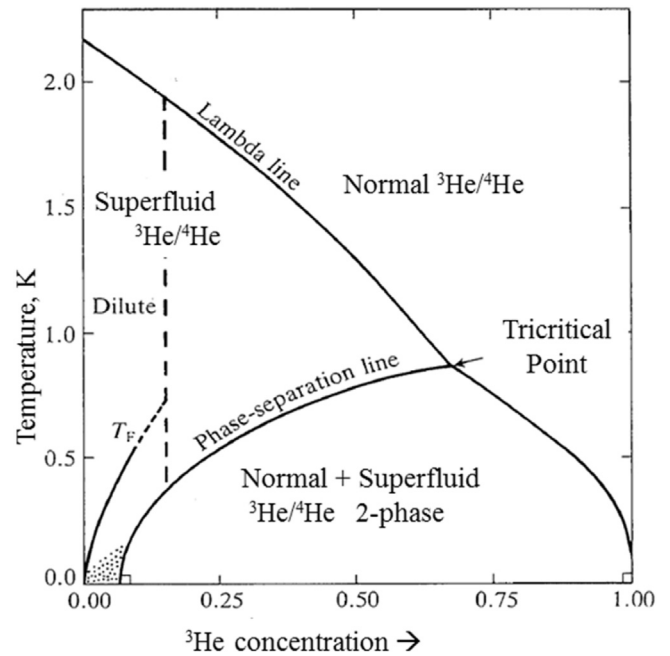


Fig. 10. Tricritical point and miscibility gap in the ^4He - ^3He binary system showing apparent residual solubility at $T = 0$ K. However, these dilute solutions of ^3He in ^4He behave as a degenerate Fermi gas at low temperature and at 0 K have zero entropy. See Ref. [42] for a more detailed discussion. After [42].

is zero as $T \rightarrow 0$ K in the Bragg-Williams approximation but not in the symmetrical ($G(\eta) = G(-\eta)$) first order Landau case.

2.4. Phase separation and ordering: ^4He - ^3He solutions

An interesting case regarding phase separation (and ordering) occurs with dilute ^3He in ^4He solutions wherein a tricritical point appears in the system at low temperatures ($T < 1.0$ K). See Fig. 10. In general, the two-phase region involves the formation of a ^4He -rich phase and a ^3He -rich phase but in the limit of $T \rightarrow 0$ K the phase separation line extrapolates to a residual solubility in apparent contradiction to the dictates of the Third Law. However, a very subtle quantum statistics effect comes into play here. At very low temperatures the dominant ^4He becomes virtually thermally inert compared to the ^3He solute in dilute solution and acts like a “thermal vacuum” in which a weakly interacting Fermi gas moves. The ^4He causes the Fermions to have an enhanced effective mass. Most importantly, the region of apparent solubility at $T = 0$ K is composed of a degenerate Fermi gas of zero entropy in accordance with the Third Law of Thermodynamics and Fermi-Dirac statistics [42].

3. Phase diagram configurations

In the foregoing discussion we primarily emphasized restrictions on the extrapolations of critical points and solvi as $T \rightarrow 0$ K in association with order \rightarrow disorder behavior and the importance of 2nd nearest-neighbor interactions in the interplay of ordering and phase separation tendencies in bringing the solution energetics in line with the Third Law. Before going into a more general discussion of phase diagrams and phase equilibria at low temperatures we call attention to some results of CVM calculations shown in Fig. 11a–b dealing with $L1_2$ and $L1_0$ ordering and predicted phase diagrams [5]. When only 1st nearest-neighbor interactions are taken into account, the results are not in accord with the Third Law but if 2nd nearest-neighbor interactions are included the calculated phase diagrams are clearly consistent with the Third Law. Interestingly, the same is true for the diagrams predicted by the Monte Carlo simulations.

Let us now look at two well-known binary systems often appearing in textbook discussions of phase diagrams. First we look at the prototypical binary isomorphous system exemplified by the Cu-Ni diagram shown in Fig. 12a [43]. The construction above 400 C shown here could not persist to $T = 0$ K because the complete solid solubility projected to 0 K would violate the Third Law since solid solutions across the diagram would have excess configurational entropy. However, the supplementary miscibility gap indicating phase separation at low temperature would allow the formation of a two-phase mixture of pure Cu and pure Ni (ferromagnetic) at 0 K and is supported by modern experimental investigations [8].

We now turn our attention to another familiar but more complex system, namely, the Cu-Zn binary phase diagram which shows a series of intermediate phases existing over a range of compositions. See Fig. 12b. The β/β' , γ and ϵ phases are essentially so-called Hume-Rothery phases [44] which are associated with certain valence electron/atom ratios. Of concern in this analysis is also the extraordinary primary solid solubility of Zn in the terminal α (fcc) phase on the Cu-rich side of the diagram. Unless the α - β/β' solvus exhibits an extraordinary topology as $T \rightarrow 0$ K we expect that the α phase will exhibit ordering and/or phase separation at low T under equilibrium conditions perhaps giving rise to a monotectoid resulting in equilibrium between pure Cu and β' at 0 K, for example. Also, there is experimental evidence that in the vicinity of 25 atomic percent Zn atomic rearrangements are occurring at low temperatures (~ 100 C) in association with the thermodynamic

constraints of the Third Law.

Turning our attention now to the γ -brass and ϵ -hcp Zn-rich phases we might expect these Hume-Rothery phase fields to constrict to ordered stoichiometric compositions at 0 K or terminate at low temperature eutectoid points. The γ -brass phase is a complex ordered cubic phase ($I\bar{4}3m$) with 52 atoms in a supercell of lattice parameter a_0 equal to approximately 0.86 nm. The ϵ -phase is hcp similar to metallic Zn and possibly ordered at low temperatures [7,8].

4. Glasses

Glass formation has been part of the discussion of the Third Law of Thermodynamics and its application to condensed matter for over 100 years. In fact, Einstein [11,14] called attention to the idea of “frozen-in” statistical disorder or residual entropy persisting to $T = 0$ K in the early twentieth century and mentioned glassy materials as systems of interest even though the structural nature of the vitreous state was not well-understood at the time. Simon [11,14] has emphasized over the years that glasses should not obey the THIRD LAW because they are non-equilibrium systems (although certain aspects or sub-systems may be in thermodynamic equilibrium and behave in accord with the Third Law of Thermodynamics). Today extensive thermodynamic and statistical mechanical studies have continued to be pursued to elucidate the nature of the glass transition particularly to reveal whether a true thermodynamic phase transition is central to glass formation. However, an important feature of this change of state is that it depends on the thermal history of the system; importantly, the onset of the glassy state at the so-called glass transition temperature (T_g) depends on the cooling rate, T_g , and is higher the faster the rate of cooling as well as the residual entropy $S' > 0$ carried to $T = 0$ K. (The reader is reminded that rate and time are not equilibrium thermodynamic variables). Here we view the glass transition as a kinetic arrest of various structural or configurational degrees of freedom of the material characterized by a spectrum of relaxation times which are “frozen” as the temperature of the metastable liquid is lowered at a finite rate. This freezing inhibits these subsystems from achieving thermodynamic equilibrium; however, some subsystems e.g the vibrational modes may be able to remain in equilibrium as $T \rightarrow 0$ K in accord with the Third Law. The vibrational subsystem might be described as an Einstein (Debye) solid allowing $C_V \rightarrow 0$ as $T \rightarrow 0$ K. Regarding the well-known Kauzmann paradox [45], it is suggested that as the entropy of the metastable liquid approaches intersection with that of the crystalline state the material essentially becomes a metastable Einstein (Debye) solid with a thermally inert structural or configurational subsystem.

Let us close our discussion of the vitreous state as a non-equilibrium state by recalling the so-called Szilard principle asserted by Leo Szilard in 1925 [46] regarding the Third Law of Thermodynamics and the “frozen-in” entropy produced by the process of glass formation. Szilard categorically states that any description of a physical or chemical system formulated in terms of thermodynamic or statistical mechanical models must be in accordance with the three laws of thermodynamics and as $T \rightarrow 0$ K must obey a generalization (or contraction) of the Third Law as modified to include non-equilibrium aspects manifest in a glass. He focused attention on the phonon and electronic contributions to the partition function of any system (liquids, crystalline solids and glasses) emphasizing in all cases as $T \rightarrow 0$ K, $S(T) \rightarrow 0$ and $C_p \rightarrow 0$ as dictated by quantum statistics and in agreement with classical thermodynamic predictions based on the inaccessibility of 0 K and the Third Law. This is in agreement with experimental results on the thermal and electrical properties of glasses in a myriad of

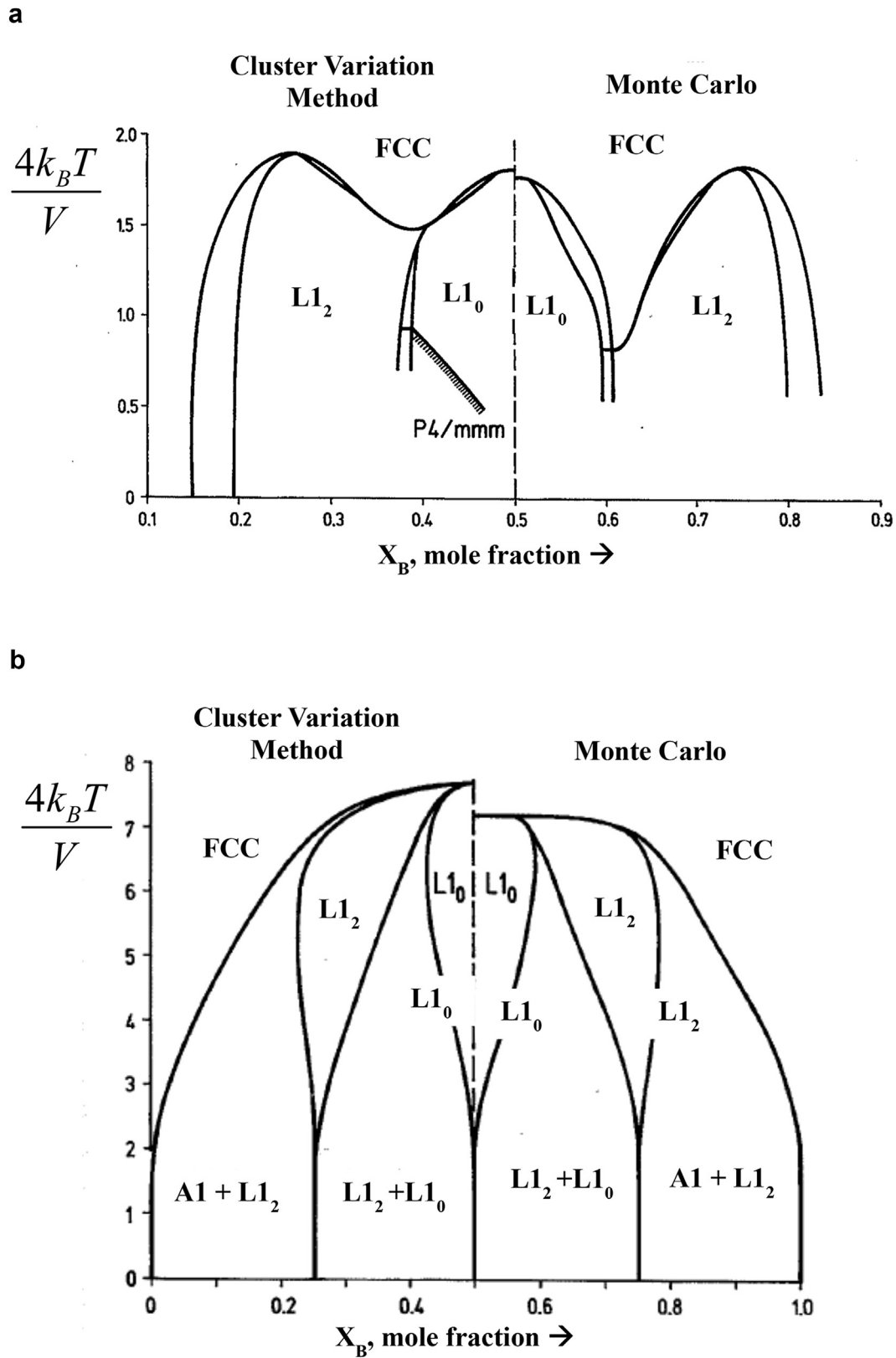
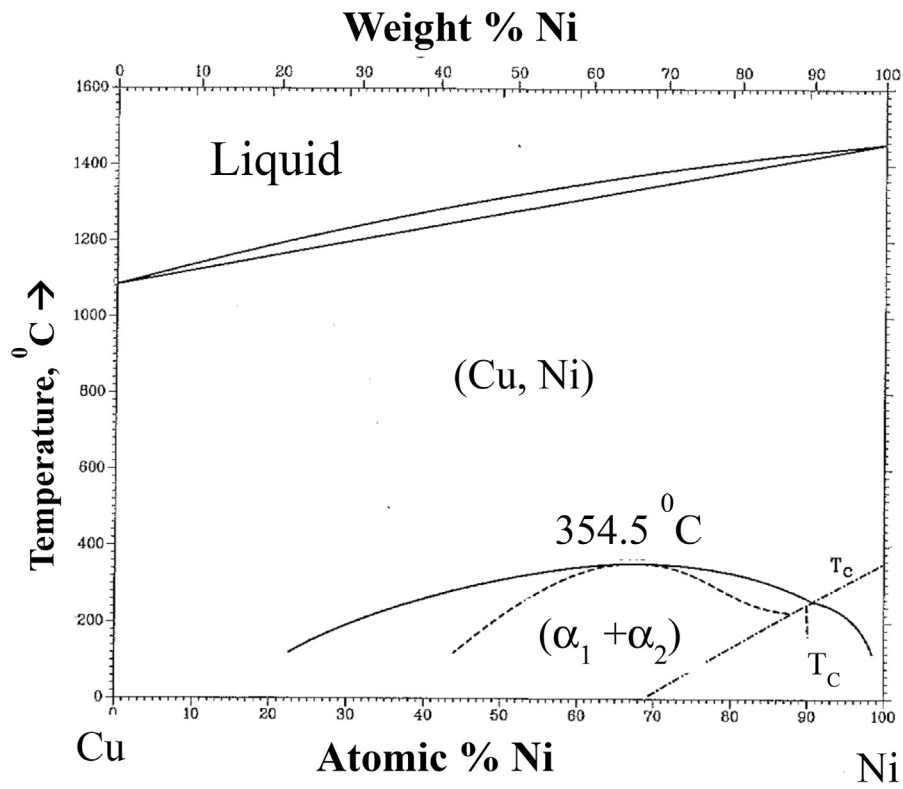


Fig. 11. a) Comparison of CVM and Monte Carlo results when only 1st nn interactions are taken into account. After [5]. b) 1st and 2nd nearest-neighbor interactions are included in the solution energetics. Clearly the results in 11a are not in accord with the THIRD LAW whereas those in 11b are. After [5].

a



b

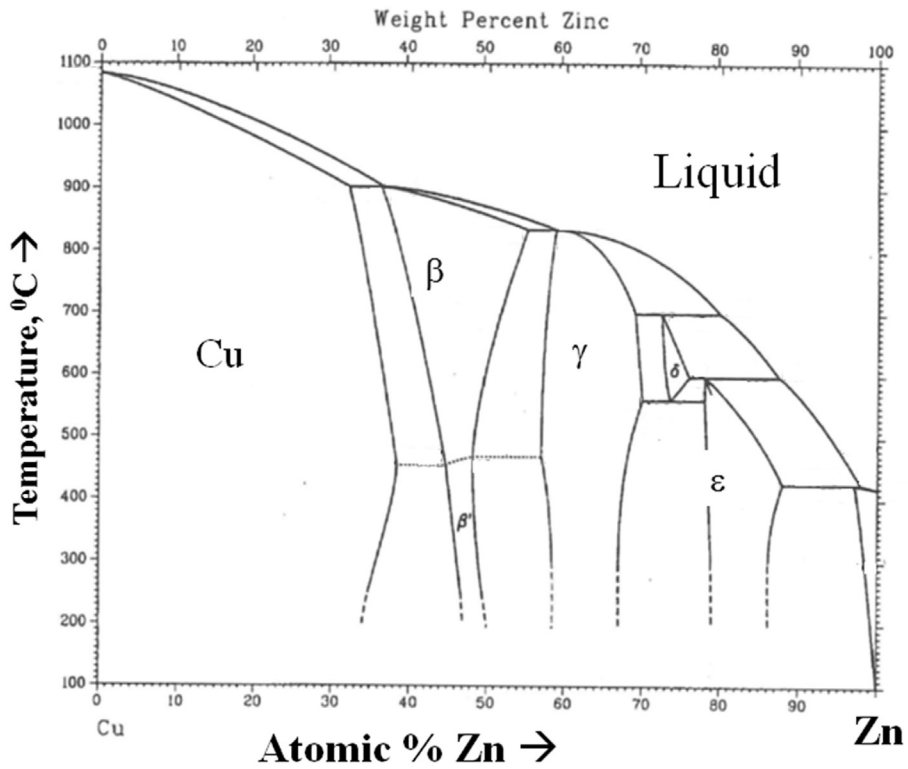


Fig. 12. a) The Cu-Ni phase diagram showing complete solid solubility above about 400C but indicating a miscibility gap at lower temperatures. After [43]. b) The Cu-Zn phase diagram showing extensive primary solid solubility in the Cu-rich region of the diagram. After [43].

specific systems. Szilard's principle received early support in von Neumann's book [47] in 1932 (emphasizing quantum mechanical considerations) and later in K.A. Putilov's [48] classical thermodynamic formulations in 1971. According to Szilard this generalized Third Law covers "frozen-in" configurational entropies and nonequilibrium systems similar to Simon's application of Third Law considerations to aspects or subsystems which are in equilibrium as discussed above. For a thorough discussion of glasses and the Third Law see Ref. [49].

5. Conclusions

The intent of this paper has been to elucidate the content of the Third Law of Thermodynamics and its role in the application of thermodynamics to phase equilibria in materials science. As noted in many discussions the Third Law differs from the FIRST and SECOND LAWS in that it introduces no new essential thermodynamic variables such as energy or entropy but importantly circumscribes the behavior of these state functions relevant to materials in such contexts as possible and required phase diagram configurations at low temperatures and consistent theoretical descriptions of alloy phase stability, ordering and phase separation. A very important contribution to the formulation of the Third Law was that due to Simon who emphasized over the years that a thermodynamic system is generally a composite of various thermal aspects or subsystems (lattice, electron gas, spins, etc.) each of which can be treated individually in terms of thermodynamic equilibrium. Some subsystems of a material may readily establish equilibrium during cooling down to 0 K within a given thermal schedule while others may not be able to achieve equilibrium at low temperatures because of their relative thermal relaxation times. The entropy of the equilibrated subsystems vanishes at $T = 0$ K in accord with the Third Law while the constrained subsystems carry residual entropy to 0 K emphasizing that the Third Law only applies to systems or subsystems in thermodynamic equilibrium. For materials in thermodynamic equilibrium at $T = 0$ K the system should be comprised of a pure phase, a mixture of pure phases and/or ordered phases with zero entropy. In early discussions of the Third Law Einstein suggested that a rigorous formulation of a Third Law required contact with the quantum theory of matter. Planck's statistical interpretation of the entropy using Boltzmann's result $S = k_B \ln W$ provided a connection, asserting that for individual phases at equilibrium at $T = 0$ K if the ground state is non-degenerate, $S_0 = 0$. (There is no rigorous theoretical formulation for this assumption). If $S_0 = 0$ (or a constant), this leads to the inaccessibility of 0 K in a finite number of cyclic processes. Finally, what is the message that the Third Law gives us regarding thermodynamic systems as they approach $T = 0$ K? One might conclude that the Third Law indicates that for any assembly of particles (or quasiparticles) within a material system or subsystem which interact – even very weakly – the particles will order at $T = 0$ K giving rise to a lowest energy ground state with $S_0 = 0$.

For further in depth discussion of various aspects of the Third Law we suggest that the reader consult the classic text by Callen [50] and the recently published text by Swendsen [51].

Acknowledgements

We wish to thank our friend and colleague Professor Armen Khachatryan for discussions over the years on the Third Law. His insights and comments have always been welcomed. The authors thank Professor Jerrold A. Floro (UVA) for his help in preparing some of the figures. We also thank the many students in our classes at Carnegie Mellon and University of Virginia for listening to and interacting with our lectures on the Third Law in our various

courses. We trust that these young Materials Scientists will adapt the concepts of this fundamental law to aspects of their research.

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