



## THE ORDER PARAMETERS AND THEIR IMPORTANCE IN MATERIALS MODELING PROBLEMS

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The order/disorder phenomenon is important in many branches of science especially metallurgy and solid state physics because the transformation is accompanied by changes in many physical properties. In the last several decades many mathematical models of Order-Parameters have been proposed by the scientific community that could better describe the phenomenon. However, due to the subtle but important differences in the definition of an 'Order Parameter', as adopted by physicists, metallurgists, chemists, thermo-dynamists, and computer scientists an odd-complexity and abstraction has unintentionally crept in. A brief review is hereby presented of the several prevailing definitions of 'Order Parameters' to highlight the use of this term as it is used in materials modeling. The work of the authors is presented that is related with predicting the pair correlations for quasi-chemical treatment of binary alloy systems. The mathematical models chosen cover the range from random to ordered solid solution.

**Keywords:** Order parameter, SRO, LRO, Pair correlations, BCC(L2<sub>0</sub>), FCC(L1<sub>2</sub>), DO<sub>3</sub>

### 1. Introduction

Since long, the word 'order' has been extensively used by the scientific community with its antonym 'disorder' equally frequently as its conjugate. With the advent of systematic studies in science, and since then, this technical phrase has gone through several metamorphoses, in its literal meaning and rigorous mathematical treatment. Because of the simplicity of the word and its frequent day-to-day usage by people of different scientific background a weird-complexity and abstraction has inadvertently been introduced. There are, in fact, subtle but important differences in its definition, as adopted by physicists, metallurgists, chemists, thermo-dynamists, and computer scientists [1-22].

The modern day user of the terminology, order parameter, especially a graduate or a postgraduate student of materials science, finds many definitions of this term confusing and perplexing. It is important that the perspective be known of the people belonging to various schools of science who use this term in as diverse meaning as a simple adjective-word or as a complex mathematical terminology. This paper is, therefore, written in two sections. In the first section the physical and

mathematical meaning of order parameter are presented. This treatment is non rigorous but effectively brings out the diversity of the usage-based definitions with particular reference to its use in materials modeling problems. The second section focuses on one particular aspect of the order parameter that is the determination of the number of like and unlike pairs in a binary solid solution which is an important area for quasi-chemical treatment of binary alloy systems. This section contains the work and results of the authors.

#### 1.1. The Scope of the Terminology Order Parameter in Materials Modeling Based on Usage

The following is a non-exhaustive list of areas covering the scope and importance of this terminology based on its usage. The detail can be seen in the references cited.

- i. as a means to differentiate between different states of matter [1].
- ii. for their importance in determining physical properties [2].
  - thermodynamic properties like configurat-

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- ional entropy and specific heat [3].
  - for predicting most of the mechanical properties [4].
  - Optical and magnetic properties [1].
- iii. in crystallography [5].
- a) for the determination of x-ray and electron diffraction intensities [5].
  - b) for determination of crystalline phases having Long Range Order (LRO) [6].
  - c) to determine order/disorder transformations [7]
- iv. for calculating the binary and higher order phase diagrams [8]
- a) in determination of pair correlations [9]
  - b) for the location of phase boundaries [10]
- v. In materials modeling [9]
- a) CALPHAD [8]
  - b) Molecular dynamics [8]
  - c) Cluster variation model (cvm) [9]
- vi. In computational-algorithm-development [11]
- vii. In statistical thermodynamics [12]

### 1.2. The Ordering Transformation in Solid Solutions

The ordering transformation in solid solutions is of practical importance. If the atoms in a substitutional solid solution are completely randomly arranged then each lattice position is available for occupation by all the constituent atoms. On the other hand, the solid solution would be called an ordered solid solution if A atoms prefer specific lattice sites (called A-sites) and B atoms prefer different but specific lattice sites (called B-sites). The three most commonly encountered ordered lattices, also referred to as super lattices are provided in Figure 1. These include BCC(L2<sub>0</sub>), FCC(L1<sub>2</sub>), DO<sub>3</sub>, for the sake of clarity the corresponding disordered lattices are also provided [7].

It is obvious that in binary alloys the number of AA, BB and AB bonds would be different in completely ordered and in completely random solid solutions. The number of AB bonds would be maximum in the completely ordered state and progressively decrease as the degree of ordering would diminish. The internal energy will depend

upon the number of bonds of each type that would vary in an ordering transformation. Many of the thermodynamic, physical, chemical and mechanical properties would change with this transformation.

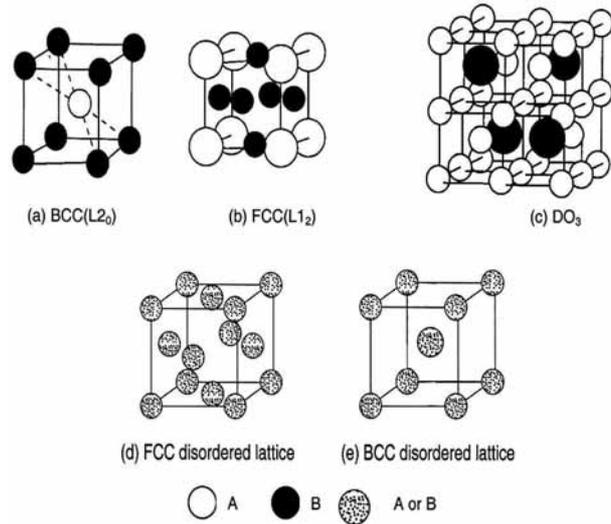


Figure 1. The BCC(L<sub>20</sub>), FCC(L<sub>12</sub>) and DO<sub>3</sub> ordered super lattices and corresponding disordered lattices.

## 2. Typical Mathematical Forms of the Order Parameters

The mathematical models of ordering were proposed soon after the discovery of x-rays. People have put forward numerous models both for SRO and for LRO

### 2.1. The SRO Parameters

Few well known equations of SRO parameters are given below

$$S = \frac{P_{AB} - P_{AB(\text{random})}}{P_{AB(\text{max})} - P_{AB(\text{random})}} \quad [13] \quad (1)$$

$$\alpha_i = 1 - \frac{p_i}{X_A} \quad [3] \quad (2)$$

$$\alpha(1) = 1 - \frac{P_{AB}(p_1)}{c_A c_B} = - \frac{\epsilon_{AB}(p_1)}{c_A c_B} \quad [14] \quad (3)$$

$$\text{SRO} = \left( \frac{P_{AB} + P_{BA}}{2} \right) - \left( \frac{P_{AB} - P_{BA}}{2} \right)^2 - X_A X_B \quad [15] \quad (4)$$

The Eq.1 is based upon the total number of bonds in a binary system of fixed size. For any superlattice, all values of  $s > 0$  indicate different level of ordering and for fully random alloys  $s = 0$ , [13].

The definition of SRO by Equation 2 characterizes the radial atomic distribution i.e. fluctuations of atomic concentrations in various coordination spheres  $i, j$  and  $k$  around an arbitrary atom that is chosen as the centre. It is implicit in this definition that there may be different values of the SRO parameter for different values of  $i$ , being the  $i^{\text{th}}$  sphere. For short range order  $\alpha_i < 0$ . This definition takes into account chemical as well as orientational order, however an-atom-by-atom positional order is not taken into account [3].

The SRO provided by Equation 3 involves the correlation parameters for different coordination spheres about an atom. It defines the correlation parameter in terms of the probability that sites of a kind occupied by A atoms are surrounded by B atoms on the other kind of sites [14].

Yet another definition of SRO is provided by Equation 4. Short-range order means that the atoms with given site fractions do not arrange themselves at random within each sublattice [15].

### 2.2. The LRO Parameters

The most well-known forms of the LRO are provided below

$$L = \frac{r_\alpha - X_A}{1 - X_A} \quad \text{where } X_A \leq r_\alpha \leq 1 \quad [13] \quad (5a)$$

$$L = \frac{r_\beta - X_B}{1 - X_B} \quad \text{where } X_B \leq r_\beta \leq 1 \quad [13] \quad (5b)$$

$$L = \frac{1}{2} \left( \frac{r_\alpha - X_A}{1 - X_A} \right) + \frac{1}{2} \left( \frac{r_\beta - X_B}{1 - X_B} \right) \quad [5] \quad (6a)$$

$$L = \frac{3}{4} \left( \frac{r_\alpha - X_A}{1 - X_A} \right) + \frac{1}{4} \left( \frac{r_\beta - X_B}{1 - X_B} \right) \quad [5] \quad (6b)$$

The Eqs. 5a and 5b describe the most widely used definition of long range order. For complete order  $L = 1$ , corresponding to  $r_\alpha = r_\beta = 1$ , and for complete randomness  $L = 0$  that would result when  $r_\alpha = X_A$  and  $r_\beta = X_B$ . It is obvious from this definition that LRO-parameter can only vary in the range  $0 \leq L \leq 1$  [13].

The LRO provided by Eqs. 6a and 6b are for AB and  $A_3B$  type lattices. In the case of an AB alloy of the body centered cubic CuZn type, the lattice can be considered as made up of two interpenetrating simple cubic lattices designated  $\alpha$  and  $\beta$ . Then the  $\alpha$  sites are arbitrarily chosen as the 'right' sites for A atoms, so that for perfect order all A atoms are on  $\alpha$  site and all B atoms are on  $\beta$  sites. In the case of alloys of near  $A_3B$  compositions the ordered lattice is composed of three simple cubic sublattices of  $\alpha$  sites and one simple cubic sublattice of  $\beta$  site [5].

### 3. Present Work

Swalin [13], has provided rigorous mathematical treatment to calculate binary pairs for the simple bcc superlattice having  $L2_0$  structure and a 50A:50B composition. In this work the same mathematical approach has been used and extended to BCC ( $L2_0$ ),  $DO_3$  and FCC( $L1_2$ ) structures. The authors have worked out the relationships between the order parameters that are defined by Equations 1, 2 and 5 to calculate the number of AA, BB and AB pairs under identical conditions. It must also be stated that Equations 1,2 and 5 are all based on unlike pairs, similar equations can easily be postulated for like pairs. The present work has demonstrated that each unique value of LRO-parameter  $L$  yields a new but fixed number of  $P_{AB}$ ,  $P_{AA}$  and  $P_{BB}$  pairs. Exactly the same number of pairs has been obtained from a different but unique value of SRO based on  $S$  or  $\alpha$ .

The assumptions made for this work include: firstly that the binary alloy contains a total of  $N_0$  atoms with no vacancies; secondly there is no composition fluctuation in the alloy and the alloy is in thermodynamic equilibrium having a minimum value of Gibbs Free Energy ( $G$ ); thirdly the mole fraction of A is  $X_A$ , hence number of A atoms is  $X_A N_0$  and lastly that the coordination number of each type of atoms is  $Z$ .

The following algorithm is used to derive the equations as shown by Swalin [13].

**Step 1:** The general formulae for the calculation of  $P_{AA}$ ,  $P_{BB}$  and  $P_{AB}$  were derived using the definition of all three order parameters, L, S and  $\alpha$ .

**Step 2:** The physically possible, precise ranges, of the three order parameters were calculated for the maximum, minimum and random number of pairs for an alloy of known composition using statistical thermodynamics.

**Step 3:** Starting with the definition of any of the order parameter (say L) and for its entire range, the numbers of binary pairs were calculated. Consequently discrete values of  $P_{AA}$ ,  $P_{BB}$  and  $P_{AB}$  for different degrees of clustering and ordering were generated

**Step 4:** For each discrete value of the binary pair (say  $P_{AB}$ ) that was calculated in step 3, the values of the two corresponding order parameters (say  $S_{AB}$  and  $\alpha_{AB}$ ) were calculated that would yield the same number of  $P_{AB}$

**Step 5:** Finally the relationship between the order parameters were determined

#### 4. Results

##### 4.1 BCC ( $L2_0$ ) Structure

The stoichiometric ratio for  $L2_0$  ordered lattice is AB. The examples of  $L2_0$  include CuZn, FeCo, NiAl, FeAl, AgMg etc [22] The coordination number Z for BCC ( $L2_0$ ) is equal to 8.

Figure 2(a-c) shows the relationship between different order parameters and predicts the number of pairs for  $L2_0$  lattice during the ordering transformations of the alloy resulting in the formation of superlattice. The following equations provide the relationship between ordering parameters for the range of LRO,  $0 \leq L \leq 1$ .

$$S_{AB} = -\alpha_{AB} = L^2 \quad (7)$$

$$S_{AA} = -\alpha_{AA} = -L^2 \quad (8)$$

$$S_{BB} = -\alpha_{BB} = -L^2 \quad (9)$$

##### 4.2 FCC ( $L1_2$ ) Structures

The stoichiometric ratio for both  $L1_2$  ordered lattices is  $AB_3$  (or  $A_3B$ ). The examples of  $L1_2$  are  $AuCu_3$ ,  $CuAu_3$ ,  $Ni_3Mn$ ,  $Ni_3Fe$ ,  $Ni_3Al$ ,  $Pt_3Fe$ , etc [22] For generalization we have taken  $X_A = 0.75$ ,  $X_B = 0.25$  with Z being the coordination number equal to 12 for  $L1_2$ .

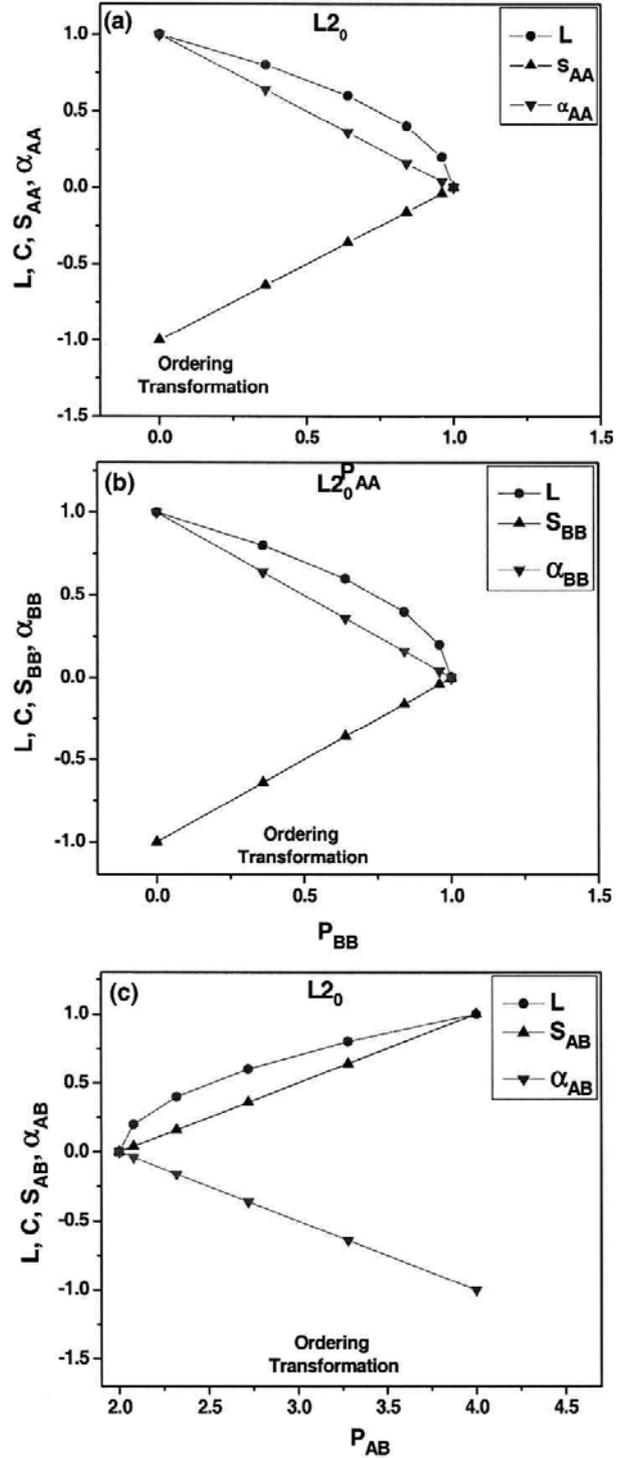


Figure 2. The relationship between different order parameters in predicting the number of pairs in BCC ( $L2_0$ ) lattice having AB composition. The figures (a-c) further predict the variation of number of  $P_{AA}$ ,  $P_{BB}$  and  $P_{AB}$  from random to ordering.

Figure 3 (a-c) shows the relationship between different order parameters in  $L_{12}$  superlattice. The

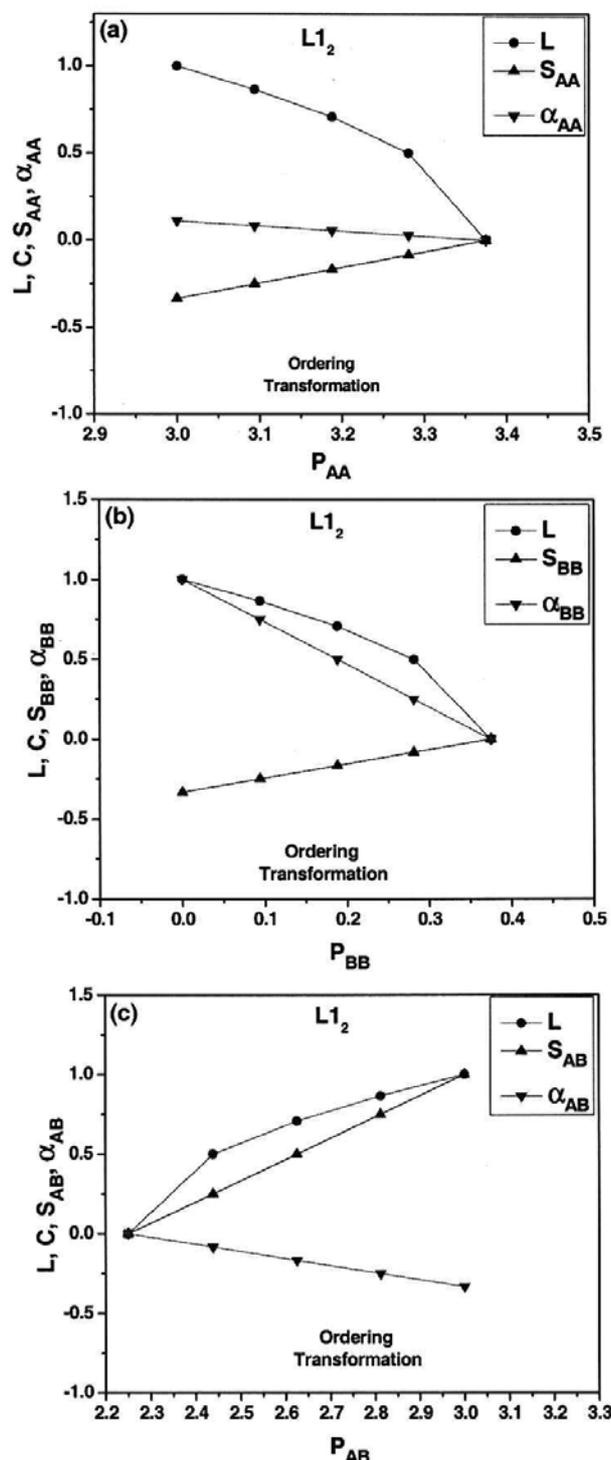


Figure 3. Order parameter relationship for FCC ( $L_{12}$ ) lattice. The typical trend of the curves in (a), (b) and (c) are due to the atomic ratio 3:1 for A and B atoms in the  $A_3B$  structure.

mathematical relationship between ordering parameters for the range of LRO,  $0 \leq L \leq 1$  are given below.

$$S_{AB} = -3\alpha_{AB} = L^2 \quad (10)$$

$$S_{AA} = -3\alpha_{AA} = -0.333L^2 \quad (11)$$

$$S_{BB} = -0.333 \alpha_{BB} = -0.333L^2 \quad (12)$$

#### 4.3 The BCC ( $DO_3$ ) Structures

The stoichiometric ratio for BCC  $DO_3$  ordered lattices is  $AB_3$  (or  $A_3B$ ). The examples of  $DO_3$  include  $Fe_3Al$ ,  $Fe_3Si$ ,  $Fe_3Be$ ,  $Cu_3Al$ ,  $BiF_3$  etc. [22]. For generalization we have taken  $X_A = 0.75$ ,  $X_B = 0.25$  with  $Z$  being the coordination number equal to 8 for  $DO_3$ .

Figure 4(a-c) shows the results for the  $DO_3$  lattice graphically while the mathematical relationship is provided in the following equations for the range of LRO,  $0 \leq L \leq 1$ .

$$S_{AB} = -3\alpha_{AB} = L^2 \quad (13)$$

$$S_{AA} = -3\alpha_{AA} = -0.333L^2 \quad (14)$$

$$S_{BB} = -0.333 \alpha_{BB} = -0.333L^2 \quad (15)$$

### 5. Discussion

It was noticed that any definition of an order parameter, be it of SRO or of LRO, can each be used for the determination of the number of AA, AB and BB pairs. This inference led to the thought that a relationship has to exist between these order parameters for the system that has a fixed number of atoms. Present work proved that this indeed was the case. The graphical representations of the derived equations are provided in Figures 2-4. It is obvious from any of these figures that a fixed number of AA, BB and AB bonds (which is a unique physical situation) fixes the value of the ordering parameter, whether it is an LRO or an SRO. Hence this work is kind of a normalization between different ordering parameters. The type of this work is exactly like determining the relationship between different temperature scales, a knowledge of which would help us to represent the melting point of ice in  $^{\circ}C$ ,  $^{\circ}F$ ,  $K$  or  $R$  without any ambiguity. It is a common practice in many problems of science and engineering to report the value of SRO or LRO for a binary system, this work is useful in predicting the number of pairs from this information, which in turn is extremely useful in determining many material properties.

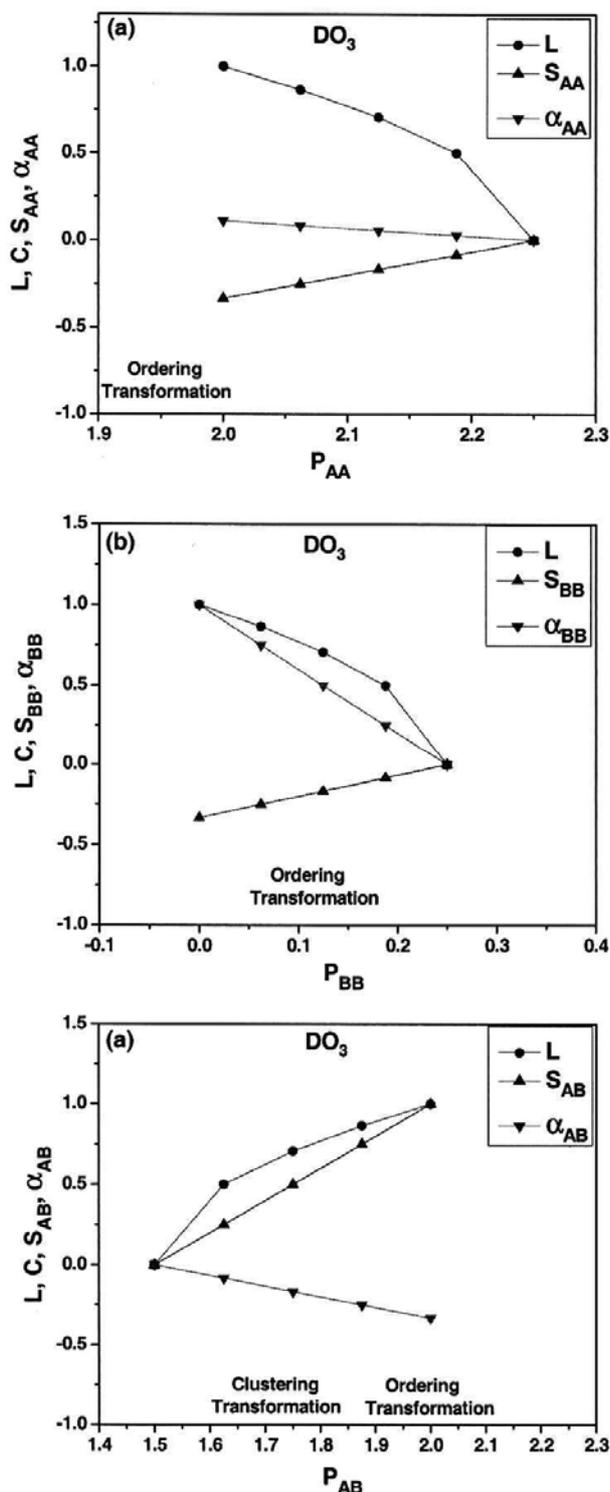


Figure 4. Like Fig. 3 but for DO<sub>3</sub> lattice having X<sub>A</sub> = 0.75 & X<sub>B</sub> = 0.25; Although the ranges of order parameters are exactly the same as in FCC L<sub>12</sub> structure but the range of each P<sub>AA</sub>, P<sub>BB</sub> and P<sub>AB</sub> are quite difficult.

All the assumptions made for this work are quite justifiable. Since the total number of pairs in N<sub>o</sub> atoms would remain constant whether the solid solution is random or ordered. The number of binary pairs would be half the number of total bonds, i.e., for a system of N<sub>o</sub> atoms with z coordination number there would be N<sub>o</sub>Z bonds but (N<sub>o</sub>Z)/2 pairs. The number of total pairs would be equal to sum of P<sub>AA</sub>+P<sub>BB</sub>+P<sub>AB</sub>. Where P<sub>AB</sub> is the number of AB+BA pairs in the system since both represent the same bond. The physical-mathematical-equation P<sub>AA</sub>+P<sub>BB</sub>+P<sub>AB</sub> = Constant, is quite unlike the purely-mathematical-equation X+Y+Z = Constant. In purely mathematical equation it is not necessary that each of X, Y and Z should have a functional relationship with each other. Each of X, Y or Z could have a positive or a negative value, not necessarily integers, and any two can be independently defined to fix the third. Even if we confine to positive integer values of X, Y and Z, still, two could be varied without considering the physical bearing on third as long as its value is a positive integer while yielding the same constant upon summation. This is not the case for P<sub>AA</sub>+P<sub>BB</sub>+P<sub>AB</sub> = Constant, where functional relationships of the type P<sub>AB</sub> = f<sub>1</sub>(P<sub>AA</sub>), P<sub>AB</sub> = f<sub>2</sub>(P<sub>BB</sub>) and P<sub>AA</sub> = f<sub>3</sub>(P<sub>BB</sub>) do exist. Hence fixing any number of either of P<sub>AA</sub>, P<sub>BB</sub>, P<sub>AB</sub> would fix the number of the other two types of pairs. This physical fact implies that there exists a relationship between order parameters as long as they are consistently defined. It is worth mentioning that the condition that there are no vacancies is also of important physical significance. In the case of vacancies there would be *vacancy plus atom pairs* that would add to the complexity of the problem.

It is concluded that the three most popular definitions of LRO and SRO can each be used to calculate the number of pairs, P<sub>AA</sub>, P<sub>BB</sub> and P<sub>AB</sub> for binary alloy solid solutions that show the phenomena of randomness or ordering under different thermodynamic conditions. This result can be generalized for all order parameters. It is also found that the relationship among order parameters between L<sub>12</sub> and DO<sub>3</sub> structures is the same but the number of pairs for both of these superlattices is quite different because of their different coordination number.

**Symbols**

S	SRO parameter notation based upon unlike AB bonds used by [21]
$P_{AB}$	The actual number of AB bonds
$P_{AB(max)}$	Maximum possible number of AB bonds
$P_{AB(random)}$	The number of AB bonds in a random solution
$S_{AB}$	SRO parameter notation used by the present authors, based upon AB bonds
$S_{AA}$	SRO parameter notation used by the present authors, based upon AA bonds
$S_{BB}$	SRO parameter notation used by the present authors, based upon BB bonds
$\alpha_i$	SRO notation based upon unlike AB bonds in the $i^{th}$ coordination sphere [3]
$P_i$	The point probability of finding B atom at position $i$
$X_A$	Mole fraction of A
$X_B$	Mole fraction of B
$\alpha_{AB}$	SRO parameter notation used by the present authors, based upon unlike AB bonds
$\alpha_{AA}$	SRO parameter notation used by the present authors, based upon unlike AA bonds
$\alpha_{BB}$	SRO parameter notation used by the present authors, based upon unlike BB bonds
$\alpha(1)$	SRO parameter used by [19]
$P_{AB(Pi)}$	Probability of finding AB pair under prior defined 'Pi' constraint
$C_A$	Concentration of atom A
$C_B$	Concentration of atom B
$\varepsilon_{AB(pi)}$	Correlation parameter for AB pair under prior defined 'Pi' constraint

L	LRO parameter notation based upon unlike AB bonds used by [21]
$r_\alpha$	Fraction of $\alpha$ sites occupied by the right atoms (A-atoms)
$r_\beta$	Fraction of $\beta$ sites occupied by the right atoms (B-atoms)

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