An analysis of the quasi-chemical model of a ternary solution: On the counting of pairs

Analiza kvazikemičnega modela ternarne raztopine: O štetju parov

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Abstract: The quasi-chemical model of a ternary solid solution was proposed in 1971 by Alex and McLellan. The model begins with the counting of different kinds of pairs between nearest atoms in a ternary crystal. The formulae of two pairs used in the model has been shown to be incorrect. A solution is suggested. A new quasi-chemical model of the solid solution developed from this work can be useful in physical metallurgy.

Izvleček: Kvazikemični model ternarne trdne raztopine sta predlagala Alex in McLellan leta 1971. Začne se s štetjem različnih vrst parov med najbližjimi atomi v ternarnem kristalu. Prikazana je nepravilna formulacija dveh parov, uporabljenih v modelu, in predlagana pravilna rešitev. Nov kvazikemični model za trdne raztopine, razvit v tem delu, je lahko uporaben v fizikalni metalurgiji.

Key words: theory; statistical mechanics; ferritic steels
Ključne besede: teorija, statistična mehanika, feritna jekla

Introduction

A statistical treatment of ternary metals, e.g. Fe-Mn(Cr,Al)-C(N,H) or Nb-Ti(V,Mo,Zr,Ta)-O(C,N), can yield thermodynamic properties which could be diffcult to obtain experimentally. As an example, the carbon-carbon interac-

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tion energy in the ferrite phase in steel can be calculated by fitting the experimentally determined Gibbs free energy to a function deduced from a simple quasi-chemical model.[1, 2] Many recent publications[3, 4] use data that are derived from the quasi-chemical model of a ternary system proposed by ALEX & MCLELLAN.[5] The current work demonstrates a fundamental problem in the model and suggests a solution, which will lead to a correct quasi-chemical model of the ternary system.

A solid phase of two or more kinds of atoms is a solid solution. The forces between the atoms in solid solution are short-ranged. Guggenheim showed that the second nearest neighbour interaction energy is negligible, if it varies as r^{-6}.[6] Most solution models consider only the nearest neighbour interactions.

The energy of a solid solution is the sum of the interaction energy of all kinds of pairs. Let us consider a binary model containing A and B atoms, and we interchange an A atom and a B atom on any two sites. Whatever the initial arrangement around the two sites, if the number of A-A pairs increases or decreases by N, then the number of B-B pairs will change by the same amount N, and the number of A-B pairs will change by $-2N$. Therefore, the properties of the solid solution depends only on the change of combined energy $N(e_{AA} + e_{BB} - 2e_{AB})$

For a non-ideal solution, i.e. $e_{AA} + e_{BB} \neq 2e_{AB}$, if $e_{AA} + e_{BB} < 2e_{AB}$, the attractive force between unlike atoms is stronger, therefore there will be a tendency for each atom to be surrounded by unlike atoms. On the other hand, if $e_{AA} + e_{BB} > 2e_{AB}$, the solution tends to segregate into A-rich and B-rich regions.

A quasi-chemical solution model accounts for the non-random distribution of atoms. It starts with the partition function , which equals the sum of all microstates the system can occupy.

$$\Omega = \sum_i \exp\left\{-\frac{E_i}{kT}\right\}$$

where k is the Boltzmann constant and $1/kT$ is the inverse temperature; E_i is the energy level of microstate i. Each microstate has a unique arrangement of atoms. Hence, E_i is the function of numbers of different pairs and associated interaction energies. Thermodynamic quantities like the Gibbs free energy and the activity of a solute can be deduced from the partition function. An exact solution of the partition function in two dimensions was obtained by ONSAGER.[7] The partition function has not been evaluated exactly for a three dimensional lattice.

The system researched in the work by Alex and McLellan contains A, B and c atoms. A and B form a substitutional solution, and may interchange positions on the sites. Whereas c atom occupy

sites in the space between the A and B atoms. It is an interstitial solute of the solvent A and B. Figure 1 shows a body-centered cubic (BCC) lattice model.

The number of A, B and c atoms are designated as N_A, N_B and N_c respectively. The ratio of interstitial sites per lattice atom is β. Therefore the number of empty sites e equals $(N_A + N_B)\,\beta - N_c$. The pairs of nearest neighbouring atoms are separated by half the lattice parameter $a/2$ and can be divided into two groups (Figure 2).

The number of nearest interstices and the number of nearest lattice atoms to any interstice are designated as Z_1 and Z_2 respectively. In the BCC structure, Z_1 equals 4, and Z_2 equals 2 (Figure 3).

The difficulty

Alex and McLellan proposed a set of formulae counting the numbers of the seven kinds of pairs for the construction of a quasi-chemical model.

For the first group of pairs, it starts with the number of pairs between atom c and site e, which is simply designated as $Z_1\lambda_1$. Then the number of c-c pairs equals the total interstitial pairs con-

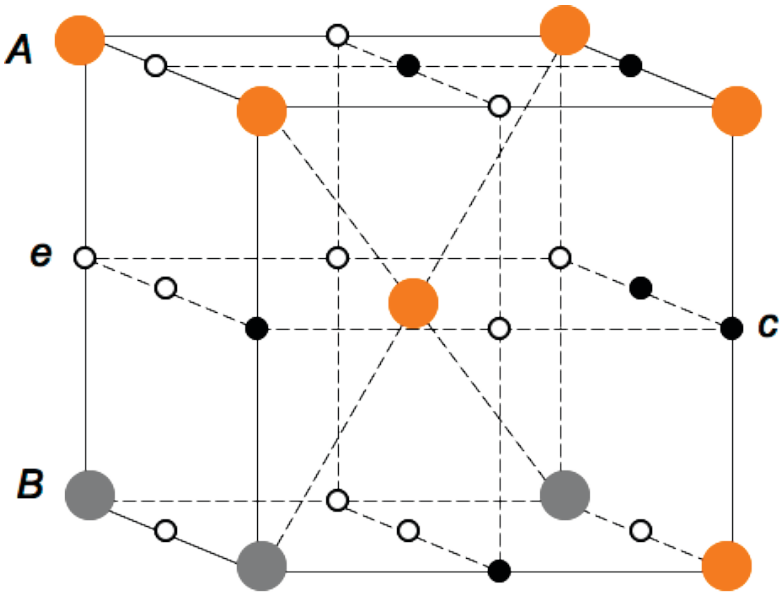

Figure 1. The ternary system consists of three types of atoms: type A, type B and type c. Atoms A and B form the BCC lattice, and atom c and empty sites e are the octahedral sites in BCC structure.

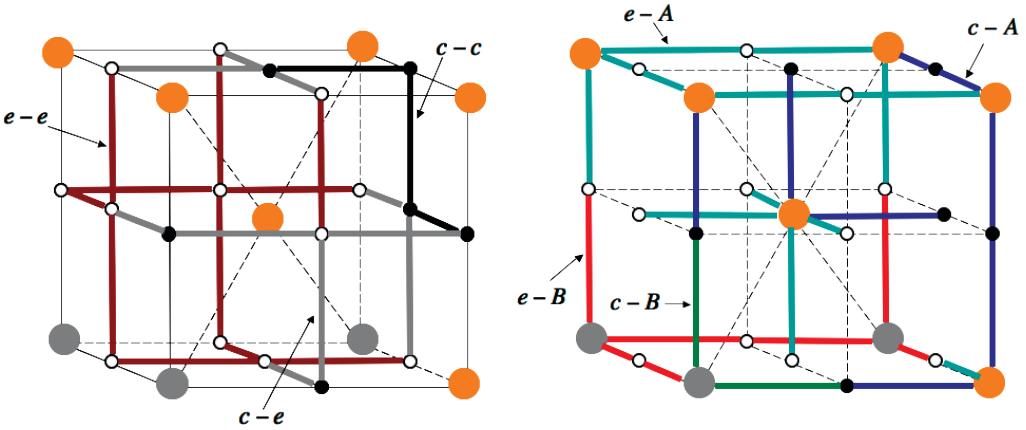

Figure 2. The left shows the pairs between interstices, i.e. c-e, c-c and e-e, and the right shows the pairs between interstice and a main lattice atom, i.e. c-A, c-B, e-A and e-B.

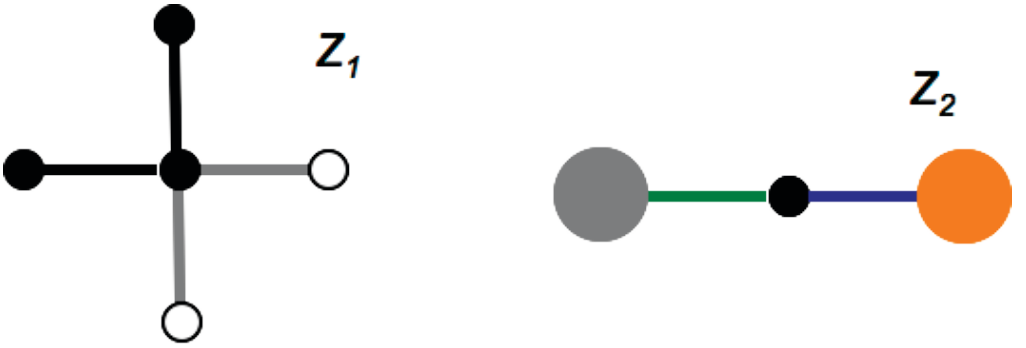

Figure 3. Z_1 is the number of nearest interstices to any interstice. Z_2 is the number of main lattice atoms to any interstice.

Table 1. Formulae of the number of pairs used in a ternary quasi-chemical model[5]

Type of pair	Count
c-e and e-c	$Z_1\lambda_1$
c-c	$(Z_1N_c - Z_1\lambda_1)/2$
e-e	$[Z_1 (N_a + N_b)\beta - (Z_1N_c - Z_1\lambda_1) - 2 Z_1\lambda_1]/2$
c-A	$Z_2\lambda_2$
c-B	$Z_2N_c - Z_2\lambda_2$
e-A	$Z_2N_a - Z_2\lambda_2$
e-B	$Z_2N_b - (Z_2N_c - Z_2\lambda_2)$

necting to c, Z_1N_c, minus those connecting c to e, and then divided by 2 as the same pair is double counted by either c of the pair. The same logic applies to the e-e pairs.

For the second group of pairs, first the number of pairs between c and A is designated as $Z_2\lambda_2$. Then the number of c-B pairs equals all the pairs connected to c minus the c-A pairs. The formulae of the numbers of e-A and e-B pairs are problematic, which will be discussed below. The list of the formulae of the counting of the pairs used by Alex & McLellan is shown on Table 1.

Let us take a closer look at the number of e-A pair and e-B pair. A simple sum of the formulae of e-A and e-B pairs in Table 1 yields the equation for the total number of pairs connecting e to A or B atoms.

$$[Z_2N_A - Z_2\lambda_2] + [Z_2N_B - (Z_2N_C - Z_2\lambda_2)] = Z_2\,(N_A + N_B) - Z_2N_C \quad (1)$$

Equation 1, in principle, should equal the number of all pairs connecting to both c and e, $Z_2\,(N_A + N_B)\beta$, minus c-A and c-B pairs

$$Z_2\,(N_A + N_B)\beta - Z_2N_c \quad (2)$$

However, clearly the two equations are not equal, as β equals 3 for a BCC lattice.

The solution

To solve the problem, a new variable, Z_3 is needed. It is the number of nearest interstices to an A atom or a B atom (Figure 4). For both body-centered cubic metal, e.g. ferrite in steel and face-centered cubic metal, e.g. austenite in steel, Z_3 equals 6.

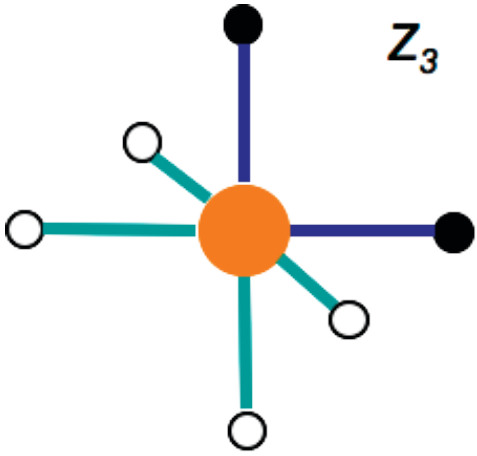

Figure 4. Z_3 is the number of nearest interstices to a lattice atom.

Table 2. The comparison of the formulae of e-A and e-B pairs.

Type of pair	Old count	New count
e-A	$Z_2N_A - Z_2\lambda_2$	$Z_3N_A - Z_2\lambda_2$
e-B	$Z_3N_B - (Z_2N_C - Z_2\lambda_2)$	$Z_2(N_A + N_B)\beta - Z_3N_A - (Z_2N_C - Z_2\lambda_2)$

The number of *e-A* pairs equals the total number of pairs connecting *A* to interstices, Z_3N_A, minus c-A pairs

$$Z_3N_A - Z_2\lambda_2$$

And the number of e-B pairs equals all the pairs connecting e to lattice atoms, $Z_2[(N_A + N_B)\beta - N_c]$, minus e-A pairs

$$Z_2[(N_A + N_B)\beta - N_c] - (Z_3N_A - Z_2\lambda_2)$$

or

$$Z_2(N_A + N_B)\beta - Z_3N_A - (Z_2N_c - Z_2\lambda_2)$$

The new and old formulae are compared in Table 2

Conclusion

A careful investigation of the quasi-chemical model of a ternary solid solution proposed by ALEX & MCLELLAN[5] has revealed a mistake in two formulae counting the number of pairs. The solution to the flaw proposed in this work will give a new quasi-chemical model of the solid solution, which will produce different functions of thermodynamic properties. It would be interesting to investigate the compatibility of the new quasi-chemical model of the ternary system with the model of a binary system[2] at the limits where $N_B \rightarrow 0$, or the interaction energy $e_{BX} \rightarrow e_{AX}$, where X represents the interstitial atom in the system.

References

[1] J. A. LOBO & G. H. GEIGER (1976): Thermodynamics and Solubility of Carbon in Ferrite and Ferritic Fe-Mo Alloys. *Metallurgical Transactions* A; 7A:1347.

[2] R. B. MCLELLAN & W. W. DUNN (1969): A Quasi-Chemical Treatment of Interstitial Solid Solutions: Its Application to Carbon Austenite. *J. Phys. Chem. Solids*; 30:2631–2637.

[3] L. M. YU, F. X. YIN & D. H. PING (2007): Natural Mechanism of the Broadened Snoek Relaxation Profile in Ternary Body-centered-cubic Alloys. *Phys. Rev. B*; 75(17):174105.

[4] M. GRUJICIC & X. W. ZHOU (1993): Monte-carlo Analysis of Short-range Order in Nitrogen-strengthened Fe-Ni-Cr-N Austenitic Alloys. *Materials Science and Engineering A*, 169:103–110.

[5] K. ALEX & R. B. MCLELLAN (1971): A Quasi-Chemical Approach to the Thermodynamics of Ternary Solid Solutions Containing Both Substitutional and Interstitial Solute Atoms. *J. Phys. Chem. Solids*; 32:449–457.

[6] E. A. GUGGENHEIM (1952): *Mixtures*. Oxford University Press, Oxford.

[7] L. ONSAGER (1944): Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition. *Phys. Rev.*; 65:117–149.