Positional Information in Solid-Solution Models

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The role of positional information in determining the thermodynamics of crystalline solid solutions is considered. It is noted that, with certain exceptions (e.g. b.c.c. Fe-B), such solutions can be classified as being exclusively either substitutional or interstitial with respect to each solute. Calculation of thermodynamic properties of interstitial solutions requires knowledge of the types of sites preferentially occupied by the solute. The problem of determining that occupancy is considered for several binary systems. A cumulant expansion technique, which meets with good success in describing dilute, high-temperature, interstitial solutions, is applied to the case of high-temperature binary substitutional systems of similar metals. The technique is shown to be of limited utility in this application.

Introduction

A certain degree of positional information always is necessary as a basic starting point in setting up any statistical-mechanical model for solid solutions. The most fundamental information concerns the basic structure of the solution, i.e. whether it is of the substitutional or interstitial type.

Even this most basic information is not always well established. A classic example is the Fe-B system. The substitutional solubility of B in b.c.c. iron is supported by lattice-parameter measurements (Strocchi, Melandri & Tamba, 1967) and the value of the migration energy (Busby & Wells, 1954) (62 kca/mole). However, internal-friction work by Thomas & Leak (1955) and by Tavadze, Bairamashvili, Metreveli & Tzagareishvili (1966) in which a Snoek peak has been found supports the interstitial sites for B in a-iron. However, other workers have failed to detect a B peak (Strocchi, Melandri & Tamba, 1967; Lucci, Della Gatta & Venturello, 1969). The recent careful internal friction study by Hayaski & Sugeno (1970) showed an internal friction peak at 50°C (due to C) and a weaker peak at -13°C which only appeared when the sample contained B. They concluded from the height of the peak at -13°C that most of the B in fact dissolved substitutionally but about a fifth of it is present in interstitial sites.

Fortunately, in most cases this kind of uncertainty is not present and the choice of interstitial or substitutional structure is clear. In the following sections we will discuss the relation between statistical models and atomic information for these two kinds of solutions.

Interstitial solutions

It has been established that to have the solute atoms in a given solid solution located in interstitial sites does not completely specify the structure of the solution since the question remains as to which particular sites are occupied. For C and N in metals there is now a large enough body of data to establish whether the tetrahedral or octahedral site in b.c.c., c.p.h., or f.c.c. solutions are predominantly occupied. However, it should be remembered that even though one site is predominantly occupied, the thermodynamic potential driving some solute atoms into a different sublattice of interstitial sites is large, especially at high tempera-
tures. This arises from the entropic term $-kT \ln \theta$ in the partial free energy $\mu$ of the solute atoms. When the ratio $\theta$ of solute to solvent atoms on a given site sublattice is small, this component of $\mu$ can be large. However, provided the difference in energy between a solute located in the two competing sites is greater than $\sim 0.25$ eV, dual site occupancy is such that the second sublattice is occupied to an extent which is not reflected in the bulk thermodynamic parameters of the solution, although it may play a major role in its kinetic behavior (McLellan, Rudee & Ishibachi, 1965).

The situation with respect to hydrogen is not as clear as for C and N. In general the scattering data are consistent with H atoms occupying the octahedral sites in f.c.c. and c.p.h. metals and the tetrahedral sites in b.c.c. metals. A fairly large volume of neutron scattering data is available for the b.c.c. Group V metals, V, Nb, and Ta. These metals absorb large amounts of hydrogen ($\theta \sim 1$) and the evidence favors tetrahedral occupancy (Langeberg & McLellan, 1973a). The ion channeling work of Carstangen & Sizmann (1972) using deuterium-doped Nb single crystals is particularly noteworthy. There are very few data for the b.c.c. and f.c.c. metals of low hydrogen occlusive capacity. Nickel is an exception and the neutron scattering work of Wollan, Cable & Koehler (1963) indicates octahedral occupancy.

It should be emphasized that this lack of positional information is a serious problem since the extraction of the thermodynamic functions of the solution from solubility data requires a knowledge of the site occupancy. For a dilute solid solution in equilibrium with $H_2$ gas of pressure $P$ and temperature $T$, the solubility can be written (Arnoult & McLellan, 1973)

$$\theta = \frac{\beta P^{1/2}}{T^{1/4}} \exp - \frac{\bar{H}_s - \frac{1}{2} E_b^0}{kT} \exp \frac{S_{ss}^u}{k}$$

(1)

where $\beta$ is the ratio of interstitial sites per solvent atom, $\bar{H}_s$ is the partial enthalpy, and $S_{ss}^u$ the partial excess entropy of the solute atoms, $-E_b^0$ is the dissociation energy of the $H_2$ molecule at 0°K, and $\lambda$ is a known constant. Thus it is essential to know $\beta$ in order to extract $S_{ss}^u$ from the temperature variation of $\theta$ at a constant pressure. In recent work on the H–Cr system (Wollan, Cable & Koehler, 1963), a value for $S_{ss}^u$ was found which, in view of the correlation of Gallagher & Oates (1969) relating $\bar{H}_s$, $S_{ss}^u$, and $\beta$, was indicative of octahedral ($\beta = 3$), rather than tetrahedral ($\beta = 6$) occupancy.

A broader question relates to the extent to which deviations from a random positioning of the solute atoms in their sites can be handled by statistical methods. The expansion of the free energy in terms of semi-invariant moments has been shown (Alex & McLellan, 1971), to be especially useful for interstitial solutions where the solubility is not large and the pairwise solute-atom interaction energy $\varepsilon_{ss}$ is such that $\varepsilon_{ss}/kT < 1$. Under such circumstances deviations from random solute distribution are not large and it has been shown that even strong second (Alex & McLellan, 1972), third (Alex & McLellan, 1973a), and more distant (Alex & McLellan, 1973b) neighbor interactions do not strongly perturb the near-random solute-atom distribution.

The very concentrated solutions of hydrogen in V, Nb, and Ta where most of the solubility data refer to relatively low temperatures (less than 1000°K) cannot, of course, be treated by high-temperature expansions. Models based on strong, but short-range, repulsive interactions between the solute atoms (Langeberg & McLellan, 1973; Buck & Alefeld, 1971; Stafford & McLellan, 1974) have been successful in explaining their thermodynamic properties and the relation between the structure of the substantially ordered b.c.c. solid solutions and the orthorhombic superlattice phases found at lower temperatures (Langeberg & McLellan, 1973; Somenkov, Gurskaya, Zernlyanov, Kost, Chernoplekov & Chertkov, 1969; Schober, Pick & Wenzel, 1973).

Substitutional solutions

There is of course a large volume of literature concerning substantially ordered substitutional solutions and the relation between ordering parameters determined from scattering experiments and statistical models.

In this report we will consider the effectiveness of applying high-temperature expansions to substitutional solutions where the departure from random mixing is relatively small. The configurational free energy can

![Fig. 1. The expansion coefficients $\lambda_i$ for f.c.c. solutions. The numbers on the curves indicate the order of the coefficients.](image-url)
be written (Krivoglaz & Smirnov, 1964; Chang, 1941) as,

\[ F^e = \frac{Z}{2} N_i (\varepsilon_{ii} - \varepsilon_{jj}) + N_j \varepsilon_{jj} - kT \ln W - kT f(C_i, \alpha) \]  

(2)

where \( Z \) is the coordination number, \( N_i \) and \( N_j \) the number of each atomic species, \( \varepsilon_{ii}, \varepsilon_{ij}, \) and \( \varepsilon_{ji} \) are the pairwise interaction energies for the pairs indicated by the subscripts, \( C_i \) is the atom fraction of the \( i \)th species, and \( \alpha \) is defined by,

\[ \alpha = \frac{2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj}}{kT} \equiv - \frac{\omega}{kT}. \]  

(3)

The quantity \( W \) is the maximum number of distinguishable configurational microstates,

\[ W = \frac{(N_i + N_j)!}{N_i!N_j!} \]  

(4)

and \( f(C_i, \alpha) \) is given by,

\[ f(C_i, \alpha) = \sum_{k=0}^{\infty} \lambda_k \frac{\alpha^k}{k!}, \]  

(5)

where the \( \lambda_k \) are combinations of the \textit{a priori} averages of the \( k \)th power of \( N_i \), the number of \( i-i \) neighbors, as have been defined previously (Alex & McLellan, 1971; Krivoglaz & Smirnov, 1964; Chang, 1941). These averages are not statistical-mechanical averages and are dependent only upon the lattice geometry and concentration of the solution and not on the energetics of mixing. Thus, equation (2) gives an exact representation of \( F^e \) within the approximations inherent in using pairwise interactions and the convergence of the series.

For f.c.c. solutions the expansion \( f(C_i, \alpha) \) has been carried out for the first four cumulants and for b.c.c. structures the first six are known (Chang, 1941). Obviously, as \( \alpha \) becomes smaller the approximation becomes more exact and we can expect meaningful results for \( \alpha \leq 1 \) especially at low concentrations.

We can relate \( F^e \) to measured thermodynamic data in the following way. The configurational chemical potential is,

\[ \mu_i^c = \frac{\partial F^e}{\partial N_i} T, V, N_j \]

\[ = \frac{Z}{2} (\varepsilon_{ij} - \varepsilon_{jj}) + kT \ln C_i + kT g(C_i, \alpha), \]  

(6)

where

\[ g(C_i, \alpha) = \sum_{k=1}^{\infty} \frac{\partial \lambda_k}{\partial N_i} T, V, N_j \frac{\alpha^k}{k!} \equiv - \sum_{k=1}^{\infty} \lambda_k \frac{\alpha^k}{k!}. \]  

(7)

Table 1. Expressions for \( \lambda_k \)

<table>
<thead>
<tr>
<th>( \lambda_k )</th>
<th>B.c.c. and simple cubic</th>
<th>F.c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_1 )</td>
<td>( \frac{1}{2}ZC^2 + ZC(1-C) )</td>
<td>( 6C^2 + 12C(1-C) )</td>
</tr>
<tr>
<td>( \lambda_2 )</td>
<td>( \frac{1}{2}ZC^3(1-C)^2 + ZC(C-1-C)^2(1-2C) )</td>
<td>( 6C^3 + 12C(1-C)^2(1-2C) )</td>
</tr>
<tr>
<td>( \lambda_3 )</td>
<td>( \frac{1}{2}ZC^4(1-C)^3 + ZC(1-C)^4(1-C) - 2C(1-6C + 6C^2) )</td>
<td>( 6C^4 + 12C(1-C)^3(1-C) - 2C(1-6C + 6C^2) )</td>
</tr>
<tr>
<td>( \lambda_4 )</td>
<td>( \frac{1}{2}ZC^5(1-C)^4(1-C) + ZC(1-C)^5(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
<td>( 6C^5 + 12C(1-C)^4(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
</tr>
<tr>
<td>( \lambda_5 )</td>
<td>( \frac{1}{2}ZC^6(1-C)^5(1-C) + ZC(1-C)^6(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
<td>( 6C^6 + 12C(1-C)^5(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
</tr>
<tr>
<td>( \lambda_6 )</td>
<td>( \frac{1}{2}ZC^7(1-C)^6(1-C) + ZC(1-C)^7(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
<td>( 6C^7 + 12C(1-C)^6(1-C) - 2C(1-6C + 6C^2) + 3(1) )</td>
</tr>
</tbody>
</table>

B.c.c.: \( Z = 8, Y = 96, J_1 = 144, J_2 = 1776 \)

Simple cubic: \( Z = 6, Y = 24, J_1 = 0, J_2 = 264 \)
The expressions for the first few $\lambda'_k$ for f.c.c. and b.c.c. solutions are given in Table 1 and plotted in Figs. 1 and 2. Now the first term in equation (6) is identical to $E_i^\infty$, the partial molar internal energy of the $i$ species in the infinitely dilute $i-j$ solution. The second term is minus the product of $T$ and the partial molar entropy of $i$ in an ideal solution $(-T S_i^d)$ so that equation (6) becomes,

$$
\mu_i = E_i^\infty - T S_i^d + k T \ln (C_i \alpha) .
$$

Since

$$
\mu_i^d = \mu_i^0 + E_i^\infty - T S_i^d
$$

then

$$
\mu_i = \mu_i^d + \mu_i^0 + k T \ln (C_i \alpha) ,
$$

where $\mu_i^0 = E_i^0 - T S_i^0$ is the free energy per mole of pure $i$. Now we note that $g(C_i, \alpha)$ vanishes at $C_i = 0$, since all $\lambda'_k$ vanish at that point. Neglecting non-configurational terms in $\mu_i$, the activity coefficient is,

$$
\frac{\mu_i - \mu_i^d}{k T \ln \gamma_i} = k T \ln \gamma_i .
$$

We see finally that,

$$
\ln \frac{\gamma_i(C_i)}{\gamma_i(0)} = + g(C_i, \alpha) .
$$

The functions $g(C_i, \alpha)$ are plotted in Figs. 3 and 4 for f.c.c. and b.c.c. solutions. In each case the order of the expansion is noted on the figure. The dashed lines correspond to taking one less term in the expansion. This has been illustrated only for the largest values of $\alpha$ (i.e. $\alpha = 1$) and it can be seen that the last term does not make a large contribution. The contributions of the final term for $\alpha < 1$ are much smaller.

From the tabulated thermodynamic data, (Hultgren, Orr, Anderson & Kelley, 1963) experimental values of $\ln [\gamma_i(C_i)/\gamma_i(0)]$ vs. $C_i$ have been plotted in Figs. 5 and 6. These binary systems were chosen because of their proximity in the periodic table and because they exhibit complete solid solubility. The values of $\omega$ obtained by fitting the experimental data to equation (12) are given in Table 2. The solute is indicated by the chemical symbol appearing first.

**Table 2. Values of $\omega$ obtained by fitting experimental data**

<table>
<thead>
<tr>
<th>Solute-solvent</th>
<th>$\alpha$</th>
<th>$T(\text{°K})$</th>
<th>$\omega(\text{kcal/mole})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuAg</td>
<td>-0.50</td>
<td>800</td>
<td>0.795</td>
</tr>
<tr>
<td>AgAu</td>
<td>-0.25</td>
<td>800</td>
<td>0.397</td>
</tr>
<tr>
<td>NiCu</td>
<td>0.15</td>
<td>973</td>
<td>-0.290</td>
</tr>
<tr>
<td>NiAu</td>
<td>0.20</td>
<td>1150</td>
<td>-0.457</td>
</tr>
<tr>
<td>CuNi</td>
<td>0.35</td>
<td>973</td>
<td>-0.677</td>
</tr>
<tr>
<td>AuNi</td>
<td>0.45</td>
<td>1150</td>
<td>-1.028</td>
</tr>
<tr>
<td>VCr</td>
<td>-0.60</td>
<td>1550</td>
<td>1.848</td>
</tr>
<tr>
<td>CrV</td>
<td>-0.10</td>
<td>1550</td>
<td>0.308</td>
</tr>
<tr>
<td>MoCr</td>
<td>0.30</td>
<td>1471</td>
<td>-0.877</td>
</tr>
<tr>
<td>MoCr</td>
<td>0.60</td>
<td>1471</td>
<td>-1.754</td>
</tr>
</tbody>
</table>

According to the model, both components behave identically in respect to $\ln [\gamma_i(C_i)/\gamma_i(0)]$. That they do not is clearly seen from Table 2.
that thermodynamic properties of the system can be described by composition-independent \( \omega \)'s specific to each atomic species and valid for a certain composition range only. However, in this case the utility of using the cumulant expansion technique instead of a simpler approach such as the parabolic representation (Darken, 1967) is doubtful.

Conclusions

The lack of adequate positional information is a barrier to the development of statistical theories of solid solutions. In the case of interstitial solid solutions the most obvious problem involves a knowledge of the sites occupied by the solute atoms. If this is not known, uncertainties are present in the extraction of thermodynamic solution parameters from the experimental solubility data.

Although the expansion of the solution free energy in terms of cumulants has proven to be of great value in treating interstitial solutions, the same cannot be said of substitutional solutions. There is a real need to build up a larger body of positional information regarding cluster formation and partial ordering in substitutional solid solutions.

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References

X-ray Diffraction Studies of Wüstite at High Temperature*

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Diffuse scattering from Fe₃O was measured at 840 °C. Relatively sharp peaks were observed along the [h00] direction near the NaCl-type fundamental peaks. The separation between these peaks and the fundamental peak corresponded to a periodicity of 2-6 times that of the NaCl-type structure in agreement with the measurement on a quenched specimen [Koch, F. & Cohen, J. B. (1969). Acta Cryst. B25, 275-287]. The peaks decreased in intensity smoothly as the composition approached the iron-rich phase boundary. However, even at the closest point to stoichiometry (x = 0.956) the peaks were still intense. Both the peak position and the half breadth of the peak were approximately constant with variation of the composition. For x = 0.900 and x = 0.956, SRO intensity was separated from the total diffuse scattering along the [h00], [hh0] and [hhh] directions. The SRO intensity consisted of the aforementioned peaks and the diffuse portion with a smooth modulation. Fourier transformation of the SRO intensity yielded positive SRO parameters for the first few shells of the octahedral cation sublattice, indicating a clustering trend within the superstructure cell (whose size was known to be on the average 2-6 times of the NaCl-type cell). A computer-simulated structure [Gehlen, P. C. & Cohen, J. B. (1965). Phys. Rev. 139, A844-A855] which was forced to fulfill the first six measured SRO parameters shows that the cation vacancies are mostly linked together with ½(110) vectors for both compositions. However no particular shape of the vacancy clusters was noticed in the simulation.

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On the Evolution of States from a Non-Equilibrium Solid Solution

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Despite the enormous variety of structural states that evolve from non-equilibrium solid solutions and despite the even larger number of models that have been proposed for them, it is becoming apparent that only a limited number of basic types of evolutionary paths exist. These are determined by considerations of thermodynamic and elastic stability, diffusion mechanisms and interface effects. For many cases, an unambiguous and detailed prediction of structural states is possible that is entirely consistent with both diffraction and imaging experiments. For other cases, strong inferences can be drawn from a few observations that drastically and verifiably limit the range of speculation. When the structure is deduced from these considerations, there are none of the special ambiguities that necessarily resulted when structural states were deduced entirely from diffraction evidence.