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CALCULATION OF THE PARTIAL STRUCTURE FACTORS IN BINARY LIQUID ALLOYS BY A THERMODYNAMICAL APPROACH

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INTRODUCTION:

The structure of the binary liquid alloys can be hardly determined experimentally. A complete information of this structure can be reached only for particular cases. Therefore, it is interesting to determine theoretically the partial structure factors (PSF). In general, the PSF obtained by the Percus-Yerick hard sphere model are not satisfactory because chemical effects are not taken into account. We have already proposed a simple method (1) to determine directly the PSF from thermodynamic properties of the mixture. This method consists in correcting the structure factor of a solvent matrix as modified by chemical interactions. We have used a statistical quasichemical treatment based on the "surrounded atom" entity in order to introduce chemical effects. Firstly, we recall this formalism and report the PSF evaluated for the Au-Li and Pb-Li systems.

1 - Quasichemical Approach.

The structure factor of the pure liquid M and the Faber-Ziman PSF of a AM liquid alloy with A dilute species are given by :

\[ a_{ij}(k) = a_{ij}(k) = 4\pi \rho \int_0^\infty (g_{ij}(r)-1) \sin(kr) r^2 dr \]

where \( \rho \) and \( \rho' \) are the average atomic densities of the liquid M and the A-M alloy respectively; \( g_{ij}(r) \) is the pair distribution function of M and \( g_{ij}(r) \) are the partial pair distribution functions in the A-M alloy. We assume that A and M have identical diameters ("substitutional hypothesis"), hence \( \rho = \rho' \). From (1) and (2) equations, we obtain the simple relations :

\[ a_{ij}(k) = a_{ij}(k) + 4\pi \rho \int_0^\infty (g_{ij}(r)-g_{ij}(r)) \sin(kr) r^2 dr \]

(3)

We introduce :

\[ g_{ij}(r) = a_{ij}(x_A,r) g_{ij}(r) \]

(4)

where \( g_{ij}(x_A,r) \) is a function describing both size effects and chemical effects and \( x_A \) is the atomic concentration of the species A. These different functions are not independent and the following relation can be easily determined :

\[ (a_{AA}(x_A,r)-1) = - \frac{x_M}{x_A} \frac{a_{AM}(x_A,r)-1}{x_A} + \frac{x_M^2}{x_A} \frac{a_{MM}(x_A,r)-1}{x_A} \]

where \( x_M \) is the atomic concentration of the solvent M. If the liquid alloy is disordered, \( a_{ij}(x_A,r)=1 \) and all three PSF are identical. For an alloy with strong chemical interactions, the parameters \( a_{ij} \) are different from one and can be considered as a measure of the local chemical order effects. To a first approximation, the chemical effects are restricted to first neighbours \( a_{ij}(x_A,r)=1 \) for \( r>a \), is the distance between first neighbours defined by \( 4\pi \rho \int_0^a g_{ij}(r) r^2 dr = z \); z is the number of nearest neighbours of an atom, taken equal to 10 in this case. Moreover any variation of \( a_{ij}(x_A,r) \) with distance \( r \) is neglected for \( 0<r<a \), consequently

\[ a_{ij}(x_A,r) = a_{ij}(x_A) \]

(5)

The parameter \( a_{AA}(x_A) \) can be evaluated from a statistical thermodynamic treatment using the "surrounded atom" model. Such a treatment allows to calculate the deviation \( \Delta x_A \) of the local composition from the mean value \( x_A \) :

\[ \Delta x_A = \frac{z(1-x_A) - \mathbb{P}}{z} \]

where \( \mathbb{P} \) is the average number of atoms M surrounding a central atom A.
\( \alpha_{AA}(x_A) \) can be easily expressed as a function of \( \Delta x_A \). In fact, the integral \( 4\pi x_A^2 \int g_{AA}(r)r^2 dr \) equals the number \( n_A \) of atom A surrounding an atom A.

Since \( g_{AA}(r) = x_A g_{AA}(x_A) = z - \bar{P} \).

Finally we obtain the relation:

\[
\alpha_{AA}(x_A) - 1 = \frac{\Delta x_A}{x_A}
\]

The FABER-ZIMAN PSF follow from (3)(4) and (5) and are given, in first order, by:

\[
a_{AA}(k) = a_m(k) + 4\pi x_A a_m(r) \sin kr r^2 dr
\]

\[
a_{AM}(k) = a_m(k) - 4\pi x_M a_m(r) \sin kr r^2 dr
\]

\[
a_{MM}(k) = a_m(k) + 4\pi x_A a_m(r) \sin kr r^2 dr
\]

For the systems AgLi and Pb-Li, RUPPERSBERG et al. have determined the PSF from X-Ray and neutron diffraction; using (6), (7) and (8) we have calculated the PSF for Ag-Li at \( x_{Ag} = 0.285 \) and for Pb-Li at \( x_{PB} = 0.38 \). In particular the first peak of all three measured PSF was found to be at the same position. This partly justifies the substitutional hypothesis for these alloys. The values of chemical local order parameter resulting from this treatment are \( \Delta x_{Ag} = -0.0373 \) for Ag\(_{0.285}\)-Li\(_{0.715}\) (using measurements by BECKER\(^4\)) and \( \Delta x_{PB} = -0.1155 \) for Pb\(_{0.38}\)-Li\(_{0.62}\) (evaluated from thermodynamic values of DEMIDOV et al.\(^5\)). The structure factor of the Li matrix has been measured at 593K by RUPPERSBERG and EGGER\(^3\). In figure 1 and 2 we compare calculated and experimental values of \( a_{ij}(k) \).

The prepeaks of the experimental PSF \( a_{Ag,Ag}(k) \) and \( a_{PB,PB}(k) \) demonstrate substantial contacts of Ag and Li, or Pb and Li, respectively due to strong heteroatomic ordering. They are stronger than those calculated, hence this chemical order effect is only partially found in the calculated PSF.

On the other hand the values of \( a_{ij}(o) \) deduced to (6) (7) and (8) are in relatively good agreement with those evaluated from thermodynamic data as shown in figure 1 and 2. This agreement is expected because chemical order parameter \( \Delta x_A \) was evaluated from a thermodynamic model. In fact \( \Delta x_A \)
should not be understood as the real deviation in concentration from the statistical mean value just at the nearest neighbour distance. It represents, instead, the deviation in concentration of the "mean field" type as averaged over longer distances. Obviously, $\Delta x_A$, as defined this way, cannot result in the correct experimental prepeak intensity, since the prepeak reflects a superstructure due to an alternation of layers enriched in atoms A and M respectively. Hence, this superstructure effect should be explained by extending chemical order effects. Therefore the quasichemical model will not be used further.

2 - CHEMICAL ORDER DAMPING EFFECT.

In order to include chemical order effects beyond the first neighbours we subdivide the space surrounding a central atom A by spherical shells and adjust their thickness to the minima of the pair distribution function of the matrix M, outside the third neighbours we choose, as period, the thickness of the third layer. In this way, we define, for each shell $i$ ($i=1,2,...,n$), the deviation of the mean concentration $x_A$ of the species A by $\Delta x_A(i)=x_A(i)-x_A$. Since the radial decay function of the chemical order parameter is not known we choose, for the sake of mathematical simplicity, a linear law: $\Delta x_A(i+1)=\alpha \Delta x_A(i)$, $\alpha$ is the so-called chemical order damping coefficient (CODC) which is positive. The negative sign reflects a periodic arrangement of the species A and M, respectively. It represents, instead, the deviation in concentration of the "mean field" type as averaged over longer distances. Obviously, $\Delta x_A$, as defined this way, cannot result in the correct experimental prepeak intensity, since the prepeak reflects a superstructure due to an alternation of layers enriched in atoms A and M respectively. Hence, this superstructure effect should be explained by extending chemical order effects. Therefore the quasichemical model will not be used further.

The extension of the previous formulation of the PSF for $n$ shells can be directly written:

$$\begin{align*}
a_{AA}(k)=a_{M}(k)+4\pi \rho \int_{a_i}^{a_{i+1}} g_M(r) \sin \frac{kr}{k} k^2 dr
\end{align*}$$

where $a_i$ and $a_{i+1}$ are the inner and outer radii of the shell $i$. We obtain similar relations for $a_{MM}(k)$ and $a_{MM}(k)$. For $k=0$, relation (12) becomes very simple:

$$a_{AA}(0)=a_{M}(0)+\frac{\Delta x_A(1)}{x_A} \sum_{i=1}^{n} (-\alpha)^{i-1} z_i$$

where $z_i$ is the number of atoms in the shell $i$. Without the knowledge of $\alpha$ and $\Delta x_A(1)$ in the first shell, we cannot directly use relation (12). In order to estimate the CODC and $\Delta x_A(1)$ we use (in equations (12) and (13)) the experimental value of the prepeak amplitude $a_{AA}(k)$ and the thermodynamic limit $a_{AA}(0)$. This treatment was applied to the liquids $\text{Ag}_{0.285}\text{Li}_{0.715}$ and $\text{Pb}_{0.38}\text{Li}_{0.62}$. On table I are reported the values of $\alpha$ and $\Delta x_A(1)$ for various $n$ values from 4 to 9. We limit the analysis of $n$ layers which approximately correspond to a distance of 25 Å from the central atom. Further the microstructure reflected by the oscillations of $r^2(g_{ij}(r)-1)$ practically disappears. Moreover, since $a_{AA}(0)$ represents the thermodynamic limit, an calculation must include a sufficiently high number of shells and consequently, results are given for $n$ values greater than 4 (corresponding to about 10 Å) only.

<table>
<thead>
<tr>
<th>$\text{Ag}<em>{0.285}\text{Li}</em>{0.715}$</th>
<th>$\text{Pb}<em>{0.38}\text{Li}</em>{0.62}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>CODC</td>
</tr>
<tr>
<td>4</td>
<td>0.1889</td>
</tr>
<tr>
<td>5</td>
<td>0.2006</td>
</tr>
<tr>
<td>6</td>
<td>0.1965</td>
</tr>
<tr>
<td>7</td>
<td>0.1975</td>
</tr>
<tr>
<td>8</td>
<td>0.1972</td>
</tr>
<tr>
<td>9</td>
<td>0.1973</td>
</tr>
</tbody>
</table>

Table I: Values of CODC and $\Delta x_A(1)$ for the liquid alloys $\text{Ag}_{0.285}\text{Li}_{0.715}$ and $\text{Pb}_{0.38}\text{Li}_{0.62}$. Note that the CODC and $\Delta x_A(1)$ are almost independent of the number $n$ of shells. This results in the relatively small value of $\alpha$ which rapidly damps the chemical order and implies that the contribution of the integrals from the fifth shell can be neglected. It should be emphasized that following the above dis-
The absolute values of $\Delta x_A^{(1)}(Ag_{0.285}Li_{0.715}) = -0.144$, $\Delta x_A^{(1)} = 0.62$, $b_{44}^{(1)} = -0.22$ are much greater than those deduced from the quasi-chemical model. BLETRY's geometrical hard sphere model (7), when applied to $Ag_{0.285}Li_{0.715}$ leads to a $\Delta x_A^{(1)}$ of $-0.17$ which is close to the one we estimated above. This agreement supports our model, in particular the estimated $\alpha$ which show that about 80% of the chemical order is localized to the first shell. The chemical order can be neglected at interatomic distances greater than 4. From $\Delta x_A^{(1)}$ and CODC, we have calculated the PSF $a_{ij}(k)$ are plotted in figure 3 and 4.

![Figure 3: Liquid Ag_{0.285}Li_{0.715}](a) $a_{Ag,Ag}$, (b) $a_{Li-Li}$, (c) $a_{Ag-Li}$

The three calculated PSF are slightly out of phase with the experimental values. This displacement is probably due to the departure from the perfect substitutional behaviour of these alloys. In fact from the diffraction measurements, RUPPERSBERG et al. have found that the distance between unlike nearest neighbours is smaller than the mean corresponding distances of the pure components. The shape of all the PSF is fairly well represented. This even applies for $a_{AM}(k)$ and $a_{MM}(k)$ which in contrast to $a_{AA}(k)$ have not been adjusted.

![Figure 4: Liquid Pb_{0.38}-Li_{0.62}](a) $a_{Pb-Pb}$, (b) $a_{Li-Li}$, (c) $a_{Pb-Li}$

CONCLUSIONS: For a dilute substitutional alloy with strong heteroatomic interactions, the knowledge of thermodynamic properties of the mixture as well as the structure factor of the matrix allows to calculate the PSF using a thermodynamical approach. We have shown that an extension of chemical order beyond first neighbours permits to explain essential experimental features of the PSF. The proposed approach is self-consistent concerning experimental PSF, thermodynamic properties and a geometrical model.

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