CHAPTER III

ON THE THERMAL EXPANSION IN $\text{AB}_3$ TYPE OR ORDERED ALLOYS
Order-disorder phenomena in binary alloy systems belong to the class of 'co-operative' phenomena of considerable intrinsic interest. Numerous metal alloy systems have substitutional solid solutions which exhibit superlattice formation near simple stoichiometric concentrations (Nix and Shockley, 1938). The theoretical investigations of the order-disorder transition in substitutional binary alloys mainly deal with the AB type of superlattice due to mathematical simplicity. The theory of the stability of superlattices as a function of temperature, was successfully developed by Bragg and Williams (1934, 35) by introducing the long-range order parameter and a reasonable refinement of Bragg-Williams approximation was made by Kirkwood (1938) in the AB type of superlattice. Following Kirkwood's method of solution, Hovi (1955) first obtained an expression for the thermal expansion coefficient for the AB type of superlattice and explained the discontinuity of expansion at the transition temperature in \( \beta \)-CuZn. In the same year (1955), Muto and Takagi extended the theoretical treatment for the AB type of superlattice to the \( AB_3 \) type in a straightforward way. In the present investigation, an expression for the thermal expansion coefficient (as a function of the long-range order parameter) in \( AB_3 \) type of binary alloys has been derived from the free energy expression as obtained by Muto and Takagi and the discontinuity of thermal expansion in ordered alloys (Cu3Au and Mg3Cd) has been explained on its basis.
THEORY

Let us consider an alloy system consisting of two types of atoms A and B with N lattice points of which $F_A N$ are $\mathcal{L}$-sites and $F_B N$ are $\beta$-sites (here $F_A$ and $F_B$ denote fractions of A atoms and B atoms respectively). It is assumed that each $\mathcal{L}$-site has $z$ neighbours all $\beta$-sites and each $\beta$-site has $z$ neighbours, of which $z F_A / F_B$ are $\mathcal{L}$-sites and $z(F_B - F_A) / F_B$ are $\beta$-sites.

In the state of perfect order, all $\mathcal{L}$-sites are occupied by A-atoms and all $\beta$-sites by B atoms. In the state of complete disorder, every lattice sites will be occupied on the average by A atoms and B atoms in proportion to their number $F_A : F_B$. In the intermediate order-states, the average distribution can be completely described by the Bragg-Williams order parameter or long-range order $'s'$ defined by:

$$s = \frac{F_L - F_A}{1 - F_A} = \frac{F_\beta - F_A}{1 - F_B}$$

where $F_L(\beta)$ is the fraction of $\mathcal{L}(\beta)$ sites occupied by A(B) atoms and $'s'$ is unity for perfect order and zero for the disordered state.

For $AB_3$ type of superlattices, with $F_A = 1/4$ and $F_B = 3/4$, Muto and Takagi (1955) considering Bragg-Williams approximation obtained in the following way an expression for the 'configurational free energy' from a generalised statistical treatment.
Expression for the Free Energy.

Let $W_{\gamma}$ represents the configurational energy of any state $\gamma$. $W_{\gamma}$ is assumed to come from the interaction energy of pairs of nearest neighbours, which seems to be a good approximation. Considering the fact shown by the quantum theory, that the forces between atoms decrease rapidly as the distance separating them increases.

Denoting the interaction energies of AA, BB and AB pairs by $-v_{AA}^* v_{BB}^*$ and the number of such pairs by $Q_{AA}$, $Q_{BB}$ and $Q_{AB}$ respectively, we get,

$$W_{\gamma} = -(Q_{AA} v_{AA}^* + Q_{BB} v_{BB}^* + Q_{AB} v_{AB}^*)$$

Now, A atoms on $<-$ sites $= r_{<} F_{AN} = (F_A + F_B s) F_{AN}$

$$\begin{align*}
\beta \quad \Rightarrow \quad \text{w}_{\beta} F_{BN} &= (1-s) F_A F_{BN} \\
\text{B} \quad \Rightarrow \quad \text{w}_{\beta} F_{BN} &= (1-s) F_B F_{BN} \\
\text{A} \quad \Rightarrow \quad \text{w}_{\beta} F_{BN} &= (F_B + F_A s) F_{BN}
\end{align*}$$

(w represents fraction of sites wrongly occupied)

The number $g(s)$ of distinguishable arrangements or configurations of atoms for the state of given $s$:

$$g(s) = \frac{[F_A N]!}{[(F_A + F_B s) F_A N]! [F_B N]!}$$
which can be rewritten, using Stirling's formula

\[
\log \left[ \frac{g(s)/N}{F_A \log F_A + F_B \log F_B - F_A (F_A + F_B s) \log [F_A (F_A + F_B s)]}
\right.
\]

\[-F_B (F_B + F_A s) \log [F_B (F_B + F_A s)]
\]

\[
= 2F_A F_B (1-s) \left[ \log F_A F_B (1-s) \right]
\]

Let us apply Bragg-William's approximation. This approximation consists essentially of replacing the true value of \( \mathbb{W}_\gamma \) (configurational energy for state \( \gamma \)) for each configuration of given \( s \) by the simple average \( \langle \mathbb{W}_\gamma \rangle \) for all states belonging to given \( s \), i.e.,

\[
\langle \mathbb{W}_\gamma \rangle = - \left\{ \langle Q_{AA} \rangle \ v_{AA}^* + \langle Q_{BB} \rangle \ v_{BB}^* + \langle Q_{AB} \rangle \ v_{AB}^* \right\}
\]

\( \langle Q_{AA} \rangle \) etc. are simple average of \( Q_{AA} \),

We find that \( AA \) pairs may result from two arrangements:

the first corresponds to one \( A \) on a \( \gamma \)-site, and the other on a \( \beta \)-site, and the second corresponds to both \( A \) atoms on \( \beta \) sites. On the average each of \( F_A N (F_A + F_B s) \) \( \gamma \)-sites occupied by \( A \) atoms have \( z(1-s)F_A \) neighbours of \( A \) atoms on \( \beta \)-sites. These are \( zN F_A^2 \) \( (1-s)(F_A + F_B s) \) of this type of \( AA \) pairs. Similarly the number of \( AA \) pairs, both of which are on \( \beta \)-sites, is found to be \( \frac{1}{2} zN F_A^2 \) \( (F_B - F_A) (1-s) \). Hence,

\[
\langle Q_{AA} \rangle = zN F_A^2 (1-s)(F_A + F_B s) + \frac{1}{2} zN F_A^2 (F_B - F_A) (1-s)^2
\]

\[
= \frac{1}{2} zN (F_A^2 - F_A s^2)
\]

(as \( F_A + F_B = 1 \))
Similarly,
\[ \langle Q_{AB} \rangle = \frac{1}{2} zN (2F_A F_B + 2 F_A^2 s^2) \]
\[ \langle Q_{BB} \rangle = \frac{1}{2} zN (F_B^2 - F_A^2 s^2) \]

Substituting these values,
\[ \langle w^\gamma \rangle = -\frac{Nz}{2} (F_A^2 v_{AA}^* + 2 F_A F_B v_{AB}^* + F_B^2 v_{BB}^*) \]
\[ -\frac{Nz}{2} F_A^2 (2v_{AB}^* - v_{AA}^* - v_{BB}^*) s^2 = \mathcal{W}(0) - NzF_A^2 v_{s2}^* \]

Let us define \( U(s) \) by,
\[ e^{-\mathcal{W}/kT} = g(s) e^{-U(s)/kT} ; \]
hence, the free energy \( F(s) = U(s) - kT \log g(s) \), using \( \langle w^\gamma \rangle = U(s) \)

Hence configurational free energy,
\[ F(s) - F(0) = NkT \left[ F_A (F_A + F_B s) \log \left( F_A (F_A + F_B s) \right) \right. \]
\[ + F_B (F_B + F_A s) \log \left( (F_B + F_A s) \right) \]
\[ \left. + 2F_A F_B (1-s) \log \left( F_A F_B (1-s) \right) \right] - 2F_A \log F_A - 2F_B \log F_B \]
\[ - Nzv_{s2}^* F_A^2 \]

Hence, for an AB_3 type of alloy, we have,
\[ F(s) - F(0) = \frac{NkT}{16} \left[ (1+3s) \log (1+3s) + 6 (1-s) \log (1-s) + (9+3s) \right] \]
\[ \log \left( 1 + \frac{s}{3} \right) - \frac{2v_{s2}^*}{kT} s^2 \] = \( F \) (say) \( \ldots (1) \)
where \( v^* = \) ordering energy = \( v_{AB}^* - (v_{AA}^* + v_{BB}^*)/2 \) and \( v^* > 0 \)

for the formation of superlattice structure.

\( k = \) Boltzmann constant; \( T = \) temperature in \( \text{OK} \).
Expression for the Thermal Expansion.

Minimizing the free energy by the condition \( \frac{\partial F}{\partial s} = 0 \) we obtain from the equation (1):

\[
K = \frac{\nu^*}{2kT} = \frac{3}{4sz} \log \frac{(1 + 3s)(1 + \frac{5}{3}s)}{(1 - s)^2}
\]  
... (2)

which gives equilibrium values of 's' at different temperatures T.

On simplification:

\[
K = \frac{4}{z} - \frac{8}{3z} s + \frac{196}{27z} s^2 - \frac{400}{27z} s^3 + \ldots \ldots
\]  
... (2a)

Differentiating equation (1) with respect to volume v and taking into account that \( \frac{\partial F}{\partial s} = 0 \), we obtain for pressure:

\[
p = -\frac{NkTz}{8} s^2 \frac{\partial K}{\partial v}
\]  
... (3)

where \( s = s(v, T) \) and \( K = K(v, T) \).

Using thermodynamic relations, it now follows from the above equation (3)

\[
\frac{\gamma}{\chi} = \left( \frac{\partial P}{\partial T} \right)_V = -\frac{NkzT}{8} \left[ s^2 \frac{\partial^2 K}{\partial v^2} + T \left\{ 2s \frac{\partial s}{\partial T} \frac{\partial K}{\partial v} + s^2 \frac{\partial^2 K}{\partial v^2} \right\} \right]
\]  
... (4)

and

\[
\frac{1}{\chi} = -v \left( \frac{\partial P}{\partial v} \right)_T = \frac{NkzT}{8} \left[ 2s \frac{\partial s}{\partial v} \frac{\partial K}{\partial v} + s^2 \frac{\partial^2 K}{\partial v^2} \right]
\]  
... (5)

where \( \gamma = \text{Thermal expansion coefficient, and } \chi = \text{compressibility.} \)

Hence, the thermal expansion coefficient:
Since, \( K = K(\varepsilon) \), alternatively,

\[
\gamma = \frac{s \frac{\partial K}{\partial S} + 2T \frac{\partial s}{\partial T} \frac{\partial K}{\partial S} + sT \frac{\partial^2 K}{\partial T^2} \frac{\partial s}{\partial S}}{2VT \frac{\partial s}{\partial V} \frac{\partial K}{\partial S} + sVT \frac{\partial^2 K}{\partial V^2} \frac{\partial s}{\partial S}}
\]  

As the transition temperature \( T_c \) is approached from low temperature, i.e. \( s \rightarrow 0 \), it follows from Exp. 2, \( \lim_{s \rightarrow 0} \frac{\partial K}{\partial S} \neq 0 \),

\( \lim_{s \rightarrow 0} \frac{\partial^2 K}{\partial s^2} \neq 0 \), and \( \lim_{s \rightarrow 0} \frac{\partial s}{\partial T} = -\infty \). From the experimental observations on Cu\(_3\)Au alloy (Owen and Liu, 1947) and Mg\(_3\)Cd alloy (Hovi and Paalassalo, 1964) it appears that volume is not discontinuous at \( T_c \) for these alloys. Now, assuming that the higher derivatives \( \frac{\partial^2 s}{\partial V^2} \) and \( \frac{\partial^2 s}{\partial T \partial V} \) remain finite as \( s \rightarrow 0 \), it follows from (7) that infinity at \( T_c \), i.e. the thermal expansion is discontinuous at the transition temperature, which had also been observed experimentally for these alloys (Siegel, 1940; Mix and MacNair, 1941; Owen and Liu, 1947 and Hovi and Paalassalo, 1964).

Temperature variation of thermal expansion in these alloys could be explained on the basis of eqn. 6 if suitable data were available.
References.


