QUALITATIVE ANALYSIS OF THE RELATIVE STABILITY OF $L_1^2(M)$ LONG-PERIOD SUPERLATTICES BASED ON THE GORSKI-BRAGG-WILLIAMS MODEL

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The stability of long-period, ordered structures and the conditions for their formation were analyzed using the $L_1^2(M)$ superlattice as an example.

If atomic ordering, i.e., the formation of long-range order in the arrangement of atoms, leads to a lowering of the syngony, then, in addition to a multiple increase in the period of translation, it necessarily is accompanied by a small deformation of the original unit cell. As a result, tetragonal $L_1^2(M)$ superlattices are formed, for example, in alloys with an initial fcc lattice. These superlattices can be obtained from $L_1^2$ by the introduction of periodic anti-phase boundaries, and consequently, are referred to as long-period relative to $L_1^2$. Superlattices with $M = 1$ and $M = 2$ have special designations: $D_{022}$ for $M = 1$, $D_{023}$ for $M = 2$; the superlattice $L_1^2$ can be represented as a superlattice with $M = \infty$.

The crystallography of long-period superlattices (LPSs) was analyzed in [1] and [2]. An analysis that considered the crystallographic superlattice and the presence of free order parameters was conducted in [3]. Low temperature conditions of stability based on general thermodynamic relationships were analyzed in [2] taking into account only the first three interaction spheres. For an fcc alloy of the composition $A_3B$, domains of stability were apparent only for the superlattices $L_1^2$ and $D_{022}$. While their broad abundance was noted experimentally in [3], the possibility of realizing other superlattices ($M \geq 2$) was not examined.

In the present study, an analysis of the possibility of different superlattices ($M \geq 1$) based on alloys with the structure $L_1^2$ was conducted within the framework of ordering theory.

As was shown in [1] and [2], the total number of order parameters in superlattices $L_1^2(M)$ is equal to $3M/2$ for even $M$, and $(3M + 1)/2$ for odd $M$. Satellite reflections $(n/M) [001]$ $(1 \leq n \leq M)$ and $(12n-1)/2M$ $(1 \leq n \leq (M + 1)/2)$ for long-period orientations along the $z$ axis correspond to these superlattices. However, the number of order parameters is substantially less in real superlattices [3]. Reflections of the type $[00n/M]$, $1 \leq n \leq M$, are always absent which implies the degeneracy of some of the order parameters, and namely the uniformity of all sites of various single-component planes (001) (Fig. 1). Also, satellites of different orders are absent. By virtue of this, almost always two, and sometimes even a single average order parameter are experimentally resolved [3]. Consequently, there is interest in the examination of superlattices of the type $L_1^2(M)$ in the approximation of double, and single order parameters.

Let us examine the basic results of the Gorskii-Bragg-Williams (GBW) theory generalized for an arbitrary number of coordination spheres, and the case of a single order parameter [4]. In this case, the free energy is given by

$$F = N[\kappa_0 \epsilon (1 - \epsilon) + \kappa_E \eta^2 - TS(\epsilon, \eta, \eta)],$$

$$\kappa_0 = \frac{1}{2} \sum_l z(l) \omega(l),$$

$$\kappa_E = \frac{1}{2} \sum_l \nu^a \nu^b \sum \omega(l) \zeta(l) \omega(l),$$

$$s = -k \left[ \nu^a (c - \nu^a) \ln (c - \nu^a \eta) + \nu^b (c + \nu^a \eta) \ln (c + \nu^b \eta) + \nu^a (1 - c + \nu^a \eta) \ln (1 - c + \nu^a \eta) + \nu^b (1 - c - \nu^a \eta) \ln (1 - c - \nu^a \eta) \right].$$

Fig. 1. The unit cells of \( \text{LI}_2(\text{M}) \) superlattices.

Here, \( c_1 \) is the concentration of the component \( \text{I} \), \( c = c_3 \); \( \nu^1 = N^1/N \) is the fraction of \( \text{i-type} \) sites, \( \nu = \nu^b \); \( z(l) \) is the coordination number in the \( l \)-th coordination sphere; \( \xi(l) = \xi^{ab}(l) + \xi^{ba}(l) - 1 \); \( \xi^{ij}(l) \) is the fraction of \( \text{i-type} \) sites in the \( l \)-th coordination sphere of a \( \text{j-type} \) site; \( \omega(l) = 2e_{\text{AB}}(l) - e_{\text{AA}}(l) - e_{\text{BB}}(l) \) is the energy of ordering in the \( l \)-th coordination sphere; \( \epsilon_{\text{LI}}(l) \) is the interaction energy of \( \text{I} \) and \( \text{J} \) atoms in the \( l \)-th coordination sphere; \( \eta = p_\text{B}^b - p_\text{A}^b \) is the order parameter; \( p_\text{A}^1 \) is the probability of finding an \( \text{i-type} \) atom on a \( \text{j-type} \) site; \( s \) is the entropy for a single atom.

Then in dimensionless form, we obtain

\[
\begin{align*}
    f &= \kappa_0 c (1 - c) + \kappa_E \eta^2 + 9\kappa_x (c, \nu, \eta), \\
    f &= \frac{F/N|\omega(1)|}{V |\omega(1)|}, \\
    \kappa_0 &= \frac{1}{2} \sum_l z(l) \omega(l), \\
    \kappa_E &= \frac{1}{2} \nu^a \nu^b \sum_l z(l) \xi(l) x(l), \\
    \kappa_x &= -3/k, \\
    x(l) &= \omega(l)/|\omega(1)|.
\end{align*}
\]

From (1) it is obvious that for a given lattice with a fixed stoichiometry (for example, a LPS with a different period), \( \kappa_E \) is a unique structure-energy parameter that characterizes a specific equilibrium superlattice. It is easy to show [4] that an equilibrium ordered superlattice can exist only for \( \kappa_E < 0 \); for a fixed \( \eta \) and a given \( c \), we obtain \( \theta \sim 1/\kappa_E \).

From this, it follows that for a fixed \( \theta \) the order parameter grows with the growth of \( |\kappa_E| \). Consequently, the corresponding changes of the energy and entropy factors introduce competing contributions into the change in the free energy. In this case, within the framework of this model, it is possible to show that the change in the entropy factor with increasing temperature cannot exceed the change in the energy factor, and cannot stabilize the structure which becomes metastable as \( \theta \to 0 \). Actually,

\[
(\delta f/\delta \eta)_\theta = (\delta f/\delta |\kappa_E|)_\theta + (\delta f/\delta \eta)_\theta (\delta |\kappa_E|/\delta \eta)_\theta.
\]

But, \( (\delta f/\delta \eta)_\theta = 0 \) (the condition for an extremum) and \( (\delta f/\delta |\kappa_E|)_\theta = -\eta^2 \). From which,

\[
(\delta f/\delta |\kappa_E|)_\theta = -\eta^2 \leq 0.
\]

Let us now examine the superlattice \( \text{LI}_2(\text{M}) \) in the approximation of a single order parameter. From Fig. 1, it is obvious that allowing for only the first coordination sphere all structures \( \text{LI}_2(\text{M}) \) are energetically equivalent. Allowing for two of the coordination spheres (\( |r(2)| = 1 \) in units of the translation period), we obtain that either the super-

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