Crystallogeometry and energy of planar superstructure defects of ternary alloys

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Abstract. Planar superstructure defects have a great influence on the mechanical and functional properties of ternary Heusler alloys; however, their complete crystallographic and energy analysis is lacking in the literature. In this work, Heusler alloys of stoichiometric composition X₂YZ of the L₂¹ superstructure are analysed. An expression is given for finding the planes of occurrence of all possible planar superstructure defects. It is established that among them there are only shear and thermal antiphase boundaries. The results obtained are useful for analyzing slip systems of the considered family of alloys and the configuration of magnetic domain walls.

1. Introduction

Among ternary alloys, a special place is occupied by the Heusler family of alloys [1, 2], which are usually defined as ternary intermetallic compounds formed with the stoichiometric composition X₂YZ with the L₂¹ structure, although these also include alloys with a large number of components and with a different symmetry [3].

Most magnetic shape memory alloys belong to the Heusler family of alloys. These are alloys based on Ni (and somewhat on the basis of Co) having an austenitic cubic phase with an L₂¹ superstructure at high temperatures and a low-symmetry phase at low temperatures, which arises as a result of martensitic transformation [4]. Martensitic transformations are responsible for the manifestation of the mechano-caloric effect [4], which consists in cooling the sample subjected to uniaxial deformation (elastocaloric effect) or volumetric deformation (barocaloric effect). Heusler alloys exhibit Seebeck and Peltier thermolectric effects [5-7]. Some rare-earth Heusler alloys exhibit a very strong magnetocaloric effect, which creates real preconditions for the development of magnetic refrigeration devices on their basis [8]. Plastic deformation leads to grain refinement in Heusler alloys, which noticeably affects their strength and physical properties.

The physical and mechanical properties of Heusler alloys are greatly influenced by planar superstructure defects. Despite the important role of planar superstructure defects in the formation of the physical and mechanical properties of Heusler alloys, there is no systematic information in the literature on the classification and energy characteristics of such defects. At the same time, there is a significant theoretical foundation, well tested on two-component ordered alloys [9-17], which makes it possible to carry out such a study for three-component Heusler alloys. Some information on the structure and energetics of various planar defects in alloys with the L₂¹ superstructure can be found in [10-15]. It seems important to give a detailed description of the coordination of atoms and possible
planar superstructure defects, as well as to calculate the energy of these defects in the hard-sphere model (without taking into account atomic relaxation).

2. Crystallogeometry and energy of planar superstructure defects

The superstructure \( L_2 \) will be represented both on the basis of a cubic translation cell with 16 atoms, and on the basis of a primitive translation cell of minimum volume with 4 atoms. Let us describe the packing of atoms in ternary Heusler alloys of stoichiometric composition \( X_2YZ \) with the superstructure \( L_2 \). As shown in figure 1, this superstructure is a union of four fcc lattices, two of which are occupied by atoms of type \( X \), one by atoms of type \( Y \), and one by atoms of type \( Z \). Each fcc lattice is a set of four simple cubic lattices, that is, the superstructure \( L_2 \) can be decomposed into 16 simple cubic gratings. Let the cubic translational cell shown in figure 1 in the Cartesian coordinate system \( xyz \), has a lattice parameter \( a \).

Figure 1. Cubic and primitive translation cells of the \( L_2 \) superstructure based on translation vectors \( w_i, i = 1,2,3 \) (highlighted in red). The cell contains two \( X \)-type atoms, one \( Y \) and one \( Z \)-type atom. The primitive cell volume is 4 times less than the cubic cell volume. The bcc lattice is based on translation vectors \( v_i, i = 1,2,3 \).

To calculate the energy of any planar superstructural defect, we delaminate the superstructure into two-dimensional monoatomic packings \( \Omega \) parallel to the orientation of the defect \((h,k,l)\):

\[
\tilde{Q} = \bigcup_{m=1}^{4} \bigcup_{\xi=-a}^{a} (P + \theta_m + \xi \mathbf{u}_3)_{s_m},
\]

where \( P \) is a two-dimensional lattice parallel to the plane of the defect, based on vectors \( \mathbf{u}_1, \mathbf{u}_2, \theta_m \) are translation vectors, \( \mathbf{u}_3 \) is a vector not lying in the plane of vectors \( \mathbf{u}_1, \mathbf{u}_2 \). Note that the vectors \( \mathbf{u}_i \) generate the lattice \( L \) in the expression. The choice of vectors \( \mathbf{u}_i \) determines the plane of the planar defect.

A planar superstructure defect is formed by joining along the plane \((h,k,l)\) of two half-crystals

\[
\tilde{Q}_+ = \bigcup_{m=1}^{4} \bigcup_{\xi=0}^{\infty} (P + \theta_m + \xi \mathbf{u}_3)_{s_m},
\]

which differ in the arrangement of types of atoms along the sublattices, and these arrangements are energetically equivalent. In (2), the subscripts “-" and “+" mark the lower and upper half-crystals. The defect energy per unit area is calculated according to

\[
E = E(\tilde{Q}_+ \leftrightarrow \tilde{Q}_-) - \frac{E}{2} (\tilde{Q}_- \leftrightarrow \tilde{Q}_+ - \tilde{Q}_+ \leftrightarrow \tilde{Q}_-) \]

where the first term on the right is the energy released when two different domains join, and the other two are the surface energy of these domains, per unit area. The first of the three energies is expressed by the following sum:

\[
E(\tilde{Q}_- \leftrightarrow \tilde{Q}_+) = \frac{1}{|\mathbf{u}_1 \times \mathbf{u}_2|} \sum_{m=1}^{4} \sum_{\eta_3=0}^{\infty} \sum_{\eta_2=0}^{\infty} \sum_{\eta_1=0}^{\infty} \phi_{s_m s_{\eta_2} s_{\eta_1}}(|r|),
\]

where \( |r| = r_{s_m} - r_{s_{\eta_2} s_{\eta_1}} = (m \theta_m + \eta_3 \mathbf{u}_3) - (n \theta_n + \eta_1 \mathbf{u}_1 + \eta_2 \mathbf{u}_2 + \eta_3 \mathbf{u}_3) \), and the multiplier before the sum normalizes the energy per unit area.
The energies \( E(\tilde{Q}_- \leftrightarrow \tilde{Q}_+) \) and \( E(\tilde{Q}_- \leftrightarrow \tilde{Q}_+) \) are calculated in the same way, but the argument of the sum will be \( \varphi_{s_m s_n}(s) \) and \( \varphi_{s_m s_n}(s) \), respectively.

Let us consider superstructure defects with different bedding planes, starting with the (001) plane. As seen from figure 1, the bundle into monoatomic two-dimensional packings parallel to the (001) plane is determined by the vectors

\[ \mathbf{u}_1 = (4,0,0), \mathbf{u}_2 = (0,2,0), \mathbf{u}_3 = (2,2,2). \]

The shift vectors will be:

\[ \mathbf{\theta}_1 = (0,0,0), \mathbf{\theta}_2 = (2,0,0), \mathbf{\theta}_3 = (1,1,1), \mathbf{\theta}_4 = (3,1,1). \]

Substituting (5) and (6) into (3) taking into account (4), we obtain the results that are presented in terms of ordering energies \( \omega_{s_m s_n} \) and energy parameters \( \Delta_{s_m s_n} \).

So, for three vectors of antiphase we have the following expressions for the energies of antiphase boundaries.

1. Case \( S_m = XXYZ, \quad S_k = XXZY \),
   \[ E = \frac{2}{a^2} (2\omega_{XY}(R_2) - 8\omega_{YZ}(R_3) + 8\omega_{YZ}(R_5) - 4\omega_{YZ}(R_6) + 24\omega_{YZ}(R_8)) \]

2. Case \( S_m = XXYZ, \quad S_k = YZZX \),
   \[ E = \frac{2}{a^2} \begin{pmatrix}
   4\omega_{XY}(R_1) + 4\omega_{XZ}(R_1) - 4\omega_{YZ}(R_1) - 4\Delta_{XY}(R_1) - 4\Delta_{XZ}(R_1) \\
   -2\omega_{XY}(R_2) - 2\omega_{XZ}(R_2) + 2\omega_{YZ}(R_2) \\
   -8\omega_{XY}(R_3) - 8\omega_{XZ}(R_3) \\
   20\omega_{XY}(R_4) + 20\omega_{XZ}(R_4) - 16\omega_{YZ}(R_4) - 12\Delta_{XY}(R_4) - 12\Delta_{XZ}(R_4) \\
   -8\omega_{XY}(R_5) - 8\omega_{XZ}(R_5) + 8\omega_{YZ}(R_5) \\
   -4\omega_{XY}(R_6) - 4\omega_{XZ}(R_6) \\
   28\omega_{XY}(R_7) + 28\omega_{XZ}(R_7) - 20\omega_{YZ}(R_7) - 12\Delta_{XY}(R_7) - 12\Delta_{XZ}(R_7) \\
   -24\omega_{XY}(R_8) - 24\omega_{XZ}(R_8) + 24\omega_{YZ}(R_8)
   \end{pmatrix} \]

3. Case \( S_m = XXYZ, \quad S_k = ZYXX \).
   Here the result is the same as in case 2.

Note that the energy of the first of the three defects is expressed in terms of the ordering energies \( \omega_{s_m s_n} \), indicating that this is a shear antiphase boundary that does not violate the stoichiometry of the alloy. At the same time, the energies of the second and third defects are not expressed only in terms of \( \omega_{s_m s_n} \), since these are thermal antiphase boundaries, leading to a local violation of stoichiometry near the boundary. This result is fully consistent with the results of the analysis of the planes of occurrence of the SAFB, where it was shown that in the plane (001) only one antiphase vector, \( \mathbf{t}_1 \), gives the SAFB, and the other two vectors do not give such a defect. Defects in the plane (011). Using the method described above, we get the following results.

1. Case \( S_m = XXYZ, \quad S_k = XXZY \),
   \[ E = \frac{2}{a^2} (4\omega_{YX}(R_2) - 14\omega_{YZ}(R_3) + 12\omega_{YZ}(R_5) - 8\omega_{YZ}(R_6) + 40\omega_{YZ}(R_8)) \]

2. Case \( S_m = XXYZ, \quad S_k = YZZX \),
   \[ E = \frac{2}{a^2} \begin{pmatrix}
   6\omega_{XY}(R_1) + 6\omega_{XZ}(R_1) - 3\omega_{YZ}(R_1) \\
   -4\omega_{XY}(R_2) - 4\omega_{XZ}(R_2) + 4\omega_{YZ}(R_2) \\
   -14\omega_{XY}(R_3) - 14\omega_{XZ}(R_3) \\
   +30\omega_{XY}(R_4) + 30\omega_{XZ}(R_4) - 15\omega_{YZ}(R_4) \\
   -12\omega_{XY}(R_5) - 12\omega_{XZ}(R_5) + 12\omega_{YZ}(R_5) \\
   -8\omega_{XY}(R_6) - 8\omega_{XZ}(R_6) \\
   +38\omega_{XY}(R_7) + 38\omega_{XZ}(R_7) - 19\omega_{YZ}(R_7) \\
   -40\omega_{XY}(R_8) - 40\omega_{XZ}(R_8) + 40\omega_{YZ}(R_8)
   \end{pmatrix} \]

3. Case \( S_m = XXYZ, \quad S_k = ZYXX \).
   Here the result is the same as in case 2.

It is worth noting that the defect energy for all three antiphase vectors is expressed through the ordering energies \( \omega_{s_m s_k} \), that is, in all three cases we have shear antiphase boundaries that do not violate the stoichiometry of the alloy. These results are consistent with the analysis of possible planes.
of occurrence of the shear antiphase boundaries, where it was shown that in the plane (011) all three vectors of antiphase, \( t_i \), give the shear antiphase boundaries.

3. Conclusions
A crystallogeometrical analysis of \( X_2YZ \) stoichiometric ternary Heusler alloys with \( L2_1 \) superstructure is presented. An expression is given for the sublimation energy of an alloy in terms of the energies of pair interactions, from which it follows that on the first coordination sphere, only the \( XY \) and \( XZ \) bonds contribute to the sublimation energy. In the second sphere, the contribution from the \( XX \) and \( YZ \) bonds appears. The \( YY \) and \( ZZ \) bonds contribute only starting from the 3rd coordination sphere.

All energetically equivalent but geometrically different representations of the \( L2_1 \) superstructure are found. It was found that all structures follow from shifts by one of the lattice vectors, while point symmetry transformations do not give new geometrically different representations of the \( L2_1 \) superstructure. On this basis, it was concluded that there are no planar superstructure defects in the \( L2_1 \) superstructure that differ from shear and thermal antiphase boundaries. Methodology developed in this study can be applied to the lattices of any dimension, in particular, to the novel 2D materials [18-22].

Acknowledgments
V.A. Valitov expresses gratitude for the financial support from the Russian Science Foundation, Grant No. 18-19-00685. This work was supported by the State Assignment of IMSP RAS No. AAAA-A17-117041310220-8.

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