THEORY OF THE ORDER-DISORDER TRANSITIONS IN THE HEUSLER ALLOYS. SUPPLEMENT

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The models of the processes of ordering of atoms in the Heusler alloys presented in the previous papers were based on extreme assumptions. Now the project of an "intermediate" model is presented. The possibilities of the experimental verification of the models of the "order-disorder" transitions are discussed.

The models of the "order-disorder" transitions in ternary cubic alloys were presented in our previous papers [1–4]. The structure of the superlattice of the alloys considered was of the $L2_1$ type (Fig. 1) in the state of complete atomic order.

At first the model of the transitions in the stoichiometrical Heusler alloys B_2AC had been elaborated [1]. It was generalized on the non-stoichiometrical alloys of the composi-

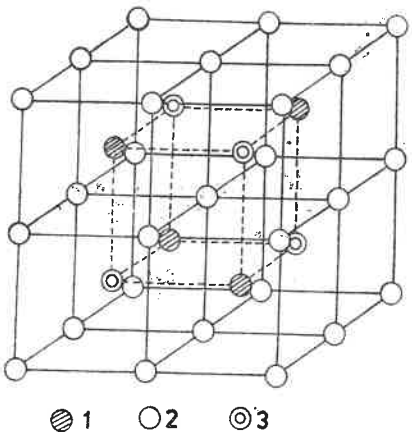

Fig. 1. The structure of the Heusler alloys

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tion $B_zA_xC_y$ [2, 3]. The generalization, however, encountered some difficulties and the additional assumptions were necessary. The problem lay in the fact that in the case of the non-stoichiometrical Heusler alloys the concentrations of atoms of the respective components differ from the fractions of the lattice points of the appropriate sublattices in the superlattice of the $L2_1$ type. However, this type of crystalline structure has been experimentally found in many ordered, non-stoichiometrical Heusler alloys [5–8]. Thus it was necessary to assume a certain distribution of the atoms of the alloy $B_zA_xC_y$ on the lattice points in the state of complete order. Two extreme cases of possible distributions of atoms were considered in our papers [2, 3]. The first model of the "order-disorder" transitions in the alloys $B_zA_xC_y$ [2] was based on the requirement that the number of lattice points in a crystal is equal to the number of atoms in an alloy. Thus in the non-stoichiometrical alloys the complete atomic order is never attained as in the whole range of temperatures there are some atoms which occupy the "unappropriate" lattice points because of the difference between the fractions of atoms and of the appropriate lattice points.

The "opposite" situation was postulated in the other model [3]. The assumption was that at a certain temperature the alloy $B_zA_xC_y$ attains a state of complete order and the deviation from the stoichiometry is compensated by the presence of the "structural vacancies" in the crystal.

Both models prove that in the Heusler alloys $B_zA_xC_y$ the ordering of atoms proceeds in two steps:

1) at the temperature T_1 the high-temperature disordered phase of the structure of the A2 type is transformed into the partially ordered one having the B2 type of structure,
2) at temperature T_2 which is lower than T_1 the phase of the B2 type of structure is transformed into another one having a structure of the type $L2_1$.

The critical temperatures T_1 and T_2 were calculated in both models. As was previously shown the above models are based on the extreme assumptions: It is possible that the ordering of atoms in the real Heusler alloys proceeds in an intermediate manner i.e. the deviation from the stoichiometry is followed both by the presence of structural vacancies in the alloy and by the abatement of the long-range order of atoms. Let us assume that the state of the maximum degree of order in the alloy $B_zA_xC_y$ may be characterized as follows:

a) the crystalline structure is of the $L2_1$ type,
b) the atoms of the component having the relatively smallest concentration occupy exclusively the lattice points of the appropriate superlattice i.e. the one, which would be occupied by these atoms if the alloy was stoichiometrical,
c) the atoms of the remaining components occupy the lattice points of the appropriate sublattices as well as a certain fraction of lattice points of other sublattices,
d) the remaining lattice points are occupied by vacancies.

As an example, the state of complete order in the alloy $B_zA_xC_y$ ($y < x < 1$) will be considered. M_1, M_2, M_3 will denote the numbers of atoms of components A, B and C in the alloy. Let us assume that the lattice points of the 2-nd sublattice (Fig. 1) are accupied by the number $M_2(1-\varepsilon)$, ($\varepsilon \geqslant 0$), of atoms of the component B and that these atoms fill the whole 2-nd sublattice. The remaining B atoms occupy the lattice points of other sub-

lattices. In accordance with the above assumptions the number N of the lattice points in the superlattice is given by the following equation:

$$N = 2M_2(1-\varepsilon).$$

Thus, one may derive the expressions for the lattice concentrations of atoms of each alloying component

$$c_1 = \frac{M_1}{N} = \frac{x}{4(1-\varepsilon)},$$

$$c_2 = \frac{M_2}{N} = \frac{1}{2(1-\varepsilon)},$$

$$c_3 = \frac{M_3}{N} = \frac{y}{4(1-\varepsilon)},$$

$$c_4 = 1-(c_1+c_2+c_3) = \frac{2-4\varepsilon-(x+y)}{4(1-\varepsilon)},$$

where c_4 denotes the lattice concentration of the "structural" vacancies.

The above formulae may be applied in further considerations of the "order-disorder" transitions in the Heusler alloys, which would be analogous to those presented in the previous paper [3]. It would be possible to express the critical temperatures of the transitions as functions of the composition of the alloy and of the parameter ε. It should be noted that the assumptions presented above are in accordance with the previous ones which were the basis of the "extreme" models [1–3]. Namely, the obvious relationship

$$c_4 \geqslant 0$$

implies that

$$0 \leqslant \varepsilon \leqslant \frac{2-(x+y)}{4}.$$

Therefore it is clear that in the case of the stoichiometrical alloy B_2AC the parameter ε is equal to zero.

The verification of which model describes the real process of the ordering of atoms in the Heusler alloys is very difficult. There are no systematic experimental data. The discovery of the defected structures in several Heusler alloys of the composition BAC [9–11] could be the case for the presence of the "structural vacancies" in the crystalline lattice. However, the smaller the deviation from the stoichiometry, the smaller is the concentration of vacancies in the alloy and it becomes impossible to ascertain experimentally if they are present in the alloy. Also the measurements of the critical temperatures of the "order--disorder" transitions are not suitable for the verification of the models. Up to now, the discovery of the phenomena of the ordering of vacancies in several alloys [9–13] has been the only information available concerning this problem.

Another difficulty encountered by the models constructed in the Bragg–Williams approximation is the impossibility of the elaboration of the model, which would contin-

uously describe alloys of any compositions. The reason for this is the discontinuity of the function of the configurational free energy at $c_i = 0$, where c_i is the lattice concentration of any alloying component. As was previously noted [3] this discontinuity results from the definition of the long-range order parameters in the Bragg–Williams approximation. These are identically equal to zero when the concentrations of the appropriate components reach zero and thus they cannot be treated as variables in such cases. However, the functions of the critical temperatures of the "order-disorder" transitions reach the finite limits at $c_i \to 0$.

Up to now, the model described in the paper [2] has been applied to calculate the critical temperatures of the "order-disorder" transitions in two series of alloys having the compositions: $Cu_2Mn_{2-y}Al_y$ $(0 \leqslant y \leqslant 1)$ and $Cu_{3-x}Mn_xAl$ $(0 \leqslant x \leqslant 1)$ and the results obtained for the latter series of compositions have been compared with the experimental data of Bouchard and Thomas [14]. The discussion was presented in our previous paper [4].

REFERENCES

[1] J. Sołtys, *Acta Phys. Pol.* **A49**, 215 (1976).
[2] J. Sołtys, *Acta Phys. Pol.* **A56**, 227 (1979).
[3] K. Sołtys, R. Kozubski, *Acta Phys. Pol.* **A56**, 235 (1979).
[4] J. Sołtys, R. Kozubski, *Acta Phys. Pol.* **A57**, 167 (1980).
[5] G. B. Johnston, E. O. Hall, *J. Phys. Chem. Solids* **29**, 193 (1968).
[6] J. P. Lisse, B. Dubois, *Mém. Sci. Rev. Mét.* **68**, 521 (1971).
[7] D. Chevereau, J. M. Gras, B. Dubois, *C. R. Acad. Sci.* (Paris) **C276**, 643 (1973).
[8] D. Chevereau, Thesis, University Paris VI (1973).
[9] G. E. Bacon, E. W. Mason, *Proc. Phys. Sol.* **92**, 713 (1967).
[10] R. H. Forster, G. B. Johnston, *J. Phys. Chem. Solids* **29**, 855 (1968).
[11] M. G. Natera, M. R. Murthy, R. J. Begun, *Phys. Status Solidi* (a) **3**, 959 (1970).
[12] R. Chang, *Scr. Metall.* **10**, 611 (1976).
[13] R. de Ridder, G. van Tendeloo, S. Amelinckx, *Phys. Status Solidi* (a) **43**, 133 (1977).
[14] M. Bouchard, G. Thomas, *Acta Metall.* **23**, 1485 (1975).