

## CONDENSED-STATE PHYSICS

### THERMOACTIVATED STRUCTURE REARRANGEMENTS IN A BINARY $\text{CuAu}_3$ ALLOY UNDER DEVIATION FROM STOICHIOMETRIC COMPOSITION

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*Thermoactivated structure rearrangements at the micro-, meso-, and macroscale levels in a binary  $\text{CuAu}_3$  alloy are investigated for the case of deviation from stoichiometry. Peculiarities of these rearrangements at the micro-, meso-, and macroscale levels are revealed.*

**Keywords:** phase transition, structure, ordered alloys.

#### INTRODUCTION

The order–disorder phase transition is one of the types of phase transitions occurring in metal alloys in condensed state. Distinguishing features of this transition are a diffuse character of the transformation and a correlation between short- and long-range ordering of atomic arrangement with the phase symmetry groups i.e., the structural features of the system. Investigation of the origin and fundamental principles of the order–disorder (O–D) transformations in metallic solid substitution solutions were initiated back in early XX century and have been pursued till now. The interest in the O–D phase transition is still profound as this transformation is quite common in metal alloys and strongly affects their properties.

There is a wealth of well-known literature, reviews and monographs, on atomic ordering and its influence on alloy properties [1–9].

The studies of ordering – disordering processes in condensed systems at the micro-, meso-, and macrolevels simultaneously have begun comparatively recently [10–14]. In [10–18], the authors investigated peculiarities of ordering – disordering for the case of high symmetry states of binary alloys (such as  $\text{Cu}_3\text{Au}$  with superstructure  $L1_2$ ) and in a classical anisotropic state (such as  $\text{CuAu}$  with superstructure  $L1_0$ ) as a function of temperature and composition. To complete investigations of ordering in a classical Cu–Au system, one has to study ordering – disordering processes in the alloy compositions close to that of  $\text{CuAu}_3$ . The classical binary system has been investigated for a long time and is illustrated by a large body of information, both theoretical and experimental, therefore to make these data complete, it is reasonable to address peculiarities of ordering – disordering in binary alloys close to an  $AB_3$  composition (such as  $\text{CuAu}_3$  with superstructure  $L1_2$ ).

Based on the diffusion nature of the O–D transition, it is natural to assume a vacancy-induced diffusion mechanism in the model. On the other hand, when setting a vacancy concentration in the model to be close to the experimental values one has to bear in mind that the simulated ordering is very fast. In order to study the details of the process, it seems useful to “decelerate” diffusion by setting a lower vacancy concentration in the model.

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If we start from a disordered state of a system, it becomes possible, using a stochastic Monte Carlo method, to obtain equilibrium configurations of the system with prescribed component concentration in a certain temperature interval.

## THE MODEL AND EXPERIMENTAL PROCEDURE

The objects under study were model binary alloys of a Cu–Au system with the following copper content: 20, 25 and 30 at. % Cu. These are fcc-alloys, with the stoichiometric alloy having an  $L1_2$  superstructure in a completely ordered state, and an  $A1$  superstructure in a disordered state.

The alloy atoms sit in the lattice nodes in accordance with the prescribed component concentrations, with the initial state being disordered. The size of the computation grid of a crystal has  $36 \times 36 \times 36$  unit fcc-lattice cells, the number of atoms  $\sim 2 \cdot 10^5$ , and use is made of periodic conditions at the grid boundaries. The temperature is set to be constant and uniform throughout the computation grid. Since during simulations of structural atomic rearrangements a vacancy-induced diffusion mechanism is assumed, so one vacancy is randomly introduced into the alloy (vacancy concentration is set to be  $\sim 0.55 \cdot 10^{-6}$ ) and two coordination spheres, as the most probable case, are used to limit the atomic hopping radius.

In a pair-interaction model, the configuration energy of a binary alloy will be given by the following:

$$E = - \sum_{i=1}^{N_s} [N_{AA}^i \phi_{AA}^i + N_{BB}^i \phi_{BB}^i + N_{AB}^i \phi_{AB}^i], \quad (1)$$

where  $\phi_{AA}^i, \phi_{BB}^i, \phi_{AB}^i$  are the opposite-sign interaction energies of the atomic pairs  $AA, BB, AB$ , respectively, at a distance equal to the radius of the  $i$ -th coordination sphere,  $N_{AA}^i, N_{BB}^i, N_{AB}^i$  is the number of the respective atom pairs in the  $i$ -th coordination sphere, and  $N_s$  is the number of interaction spheres taken into consideration.

From the initial disordered state of the system we obtained, using a stochastic Monte Carlo method, equilibrium configurations with predetermined component concentrations within a certain temperature range. The state of the alloy was taken to be equilibrium and stable, if the parameters characterizing the system (energy, order parameter, entropy) remained constant for an arbitrary long time; note that the system was not allowed to change this state without an external action. While a conventionally used criterion of equilibrium is that of achieving an extremum of one of the macroscopic characteristics, in our approach the exact dynamic behavior of the system is replaced by its discrete states, with every iteration step corresponding to one act of atomic vacancy-induced self-diffusion. It should be noted that in every iteration step we calculate the probability of one of the atoms found in the vicinity of a vacant site to occupy it, with the probability of an atom  $i$  hopping into a vacant lattice site  $j$  being an exponential function of temperature

$$P_{ij} = A \cdot \exp\left(-(\Delta E_{\max} - \Delta E_v^{ij}) / kT\right). \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $A$  is the normalization factor ensuring that the normalization condition is fulfilled (the sum of probabilities of hopping for the atoms located in the first and second coordination spheres with respect to the site is equal to unity, i.e.,  $\sum_{ij}^n P_{ij} = 1$ , where  $n$  is the number of atoms in the first and second coordination spheres with respect to the vacancy). The value of released (deposited) energy  $\Delta E_v^{ij}$  is estimated for every atom  $i$  surrounding the vacancy  $j$  in the first and second coordination spheres, it is equal to the difference between the bonding energy of the atom  $i$  in the vacant site position  $E_k^{ij}$  and the bonding energy of the atom  $i$  in the position prior to hopping  $E_n^{ij}$ : i.e.,  $\Delta E_v^{ij} = E_k^{ij} - E_n^{ij}$ . As a result, from all the values of  $\Delta E_v^{ij}$  we select the maximum value denoted as  $\Delta E_{\max}$ .

In order to identify the phases formed in the course of structural changes (here  $A_3B$ ,  $AB$ ,  $AB_3$  and those of pure components), we used an approach based on determining the number of atomic pair bonds in the first coordination sphere corresponding to each structure formed [10, 11]. This implies that the  $A_3B$  phase structure is found for an  $A$  kind atom as the number of its bonds in the first sphere  $A-A$ , which is equal to 4, and  $A-B = 8$ , while for the  $B$  kind atom the number of bonds  $A-B$  is 12. For an  $A$  kind atom, the  $AB$  phase structure would control the number of bonds in the first sphere  $A-A$ , which is equal to 4, and  $A-B = 8$ , while for the  $B$  kind atom  $B-B$  is equal to 4 and  $A-B = 8$ . For a  $B$  kind atom, the  $AB_3$  phase structure controls the number of its bonds in the first sphere  $B-B$ , which is equal to 4, and  $A-B = 8$ , while for an  $A$  kind atom the number of bonds  $A-B$  is 12. For pure component phases, the number of bonds in the first coordination sphere of similar components is equal to the number of atoms in the first coordination sphere, i.e., 12.

In order to describe the changes in the alloy state, we made use of such notions as domain, cluster, and phase- and antiphase boundaries. In the text below, an ordered phase will be described by the number, size, and shape of domain structures, with the domains corresponding to the parts of a crystal ordered as CuAu (superstructure  $L1_0$ ). Note that the domains are likely to have different orientation and to be shifted with respect to each other. The latter are referred to as antiphase domains. An  $L1_2$  superstructure can have four such domains differing in the position of the atom of the second component in the superlattice unit cell. Let us take a cluster to represent a disordered structure and to contain atoms of different kind, whose number of pair bonds in the first coordination sphere would not correspond to that in the ordered  $A_3B$  phase. The disordered phase consists of cluster atoms and substitution point defects. The interface between two antiphase domains will be denoted here as an antiphase boundary, and the region separating the ordered and disordered phases shall be referred to as a phase boundary. A “semi-ordered” phase would contain both antiphase and phase boundaries.

To verify the resulting model and the experimental procedure, it is useful to carry out a comparative testing of the well-established mechanisms and the respective dependences obtained within the proposed model and the procedure used. The parameters for this purpose were well-known lattice parameters and lattice tetragonality values, as well as short- and long-range order parameters, all taken as a function of temperature.

It is well known [17] that a measure of short-range ordering is the ratio of  $N_n^{AB}$  (number of pairs of  $A$  and  $B$  atoms spaced by a distance equal to the radius of the  $n$ -th coordination sphere) to the number of  $A$  and  $B$  atoms that would be in these positions, given their completely chaotic distribution over the lattice sites, i.e.,

$$\sigma_n^{AB} = 1 - \frac{P_n^{AB}}{C_B}, \quad (3)$$

where  $P_n^{AB}$  is the probability of finding a  $B$  atom in the  $n$ -th coordination sphere, given that an  $A$  atom is located in the central site.

The long-range ordering degree [18] is proportional to the deviation  $P_A^{(1)}$  (probability that atom  $A$  is found in its sub-lattice) from  $C_A$  (concentration of  $A$  atoms in the alloy)

$$\eta = \frac{P_A^{(1)} - C_A}{1 - \nu}, \quad (4)$$

where the probability  $P_A^{(1)} = \frac{N_A^{(1)}}{N^{(1)}}$  is equal to the number of  $A$  atoms, sitting in their site, to the number of sites in the first sub-lattice, in this case  $\nu = 3/4$ .

Free energy was determined as a function of long-range ordering [18]:

$$F = E - TS(\eta), \quad (5)$$

where  $T$  is the temperature and  $S$  is the configurational entropy.

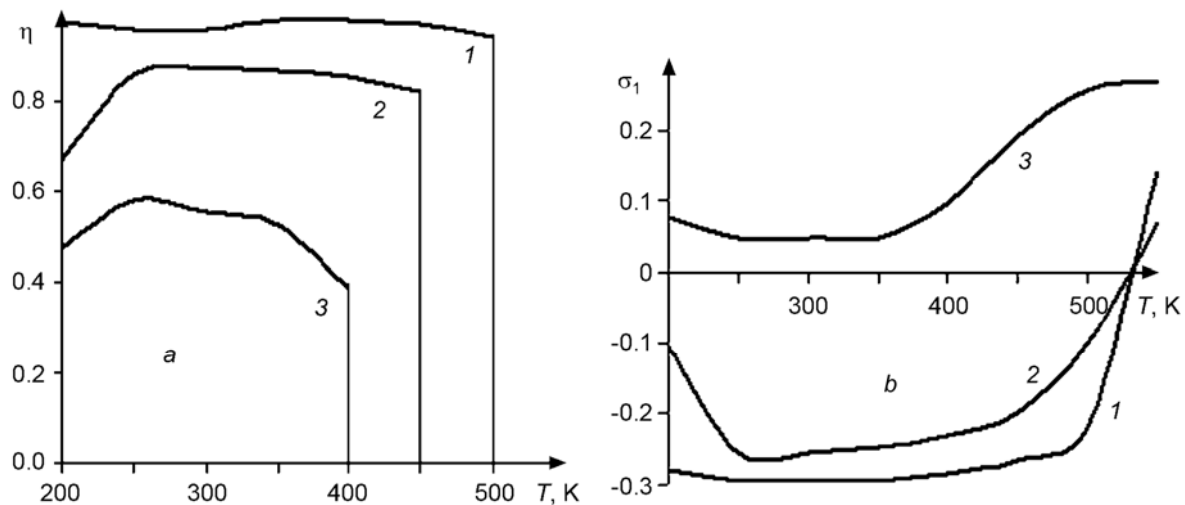


Fig. 1. Temperature dependence of long- (a) and short-range order parameter (b) in the alloys with: 25 at.% Cu (curve 1), 30 at.% Cu (curve 2), and 20 at.% Cu (curve 3).

## RESULTS AND DISCUSSION

To study thermoactivated atomic-structure rearrangement in the alloy, we performed a computer experiment using the following scheme. In the first step of simulation, we formed three types of initial crystal blocks, then introduced a vacancy into each of them, which yielded a vacancy concentration of  $0.55 \cdot 10^{-6}$ . After that, we prescribed the temperature and, using a Monte Carlo method, activated the vacancy diffusion mechanism of atoms. It should be noted that the atomic interaction energy was tabulated from the distance to three coordination spheres using the Morse potential function and its parameters from [19]. Thermoactivation of the system was performed in a stepwise fashion within the temperature range from 200 to 500 K with a step of  $\Delta T = 50$  K using  $10^8$  iterations for every temperature value in the three computation blocks. At low temperatures, we observed the process of ordering, while at higher temperatures after a certain ordered state, depending on the alloy composition, was achieved, the system was observed to disorder.

**Behavior of long- and short-range order parameters.** Figure 1a plots the long-range order parameter versus temperature. It is evident that its lowest value and a drop to zero is observed at the copper concentration 20 at.% (curve 3), with its values varying from 0.6 to 0 within the temperature interval 250–400 K. As the copper content is increased to 30 at.%, the long-range order parameter changes less abruptly from 0.86 to 0 within the temperature range 250–500 K (curve 2). For the stoichiometric alloy, the long-range order parameter is close to unity up to 500 K (curve 1).

The behavior of the short-range order parameter as concerns the temperature and component composition correlates fairly well with that of the long-range order parameter. In the alloy with 20 at.% Cu, the short-range order parameter is positive and increases with temperature from 0.05 to 0.25; but for an elevated copper content of 25 and 30 at.% it is negative up to the temperature 500 K, which testifies of a tendency to ordering in these alloys. It is clearly seen that the most ordered state is found in the stoichiometric alloy (curve 1), which persists up to very high temperatures. The temperature of the O–D phase transition in the alloy of stoichiometric composition is higher than the critical temperature in the alloy with a lower copper concentration and comparable with the phase transition temperature in the alloy with a higher copper content. For the case of deviation from stoichiometry, a more ordered state was observed in the alloy with 30 at.% Cu (curve 2) compared to that in the alloy with 20 at.% Cu (curve 3). The temperature of the order–disorder phase transition in the alloy with 20 at.% Cu is lower than that in the alloys of stoichiometric composition and elevated copper concentration.

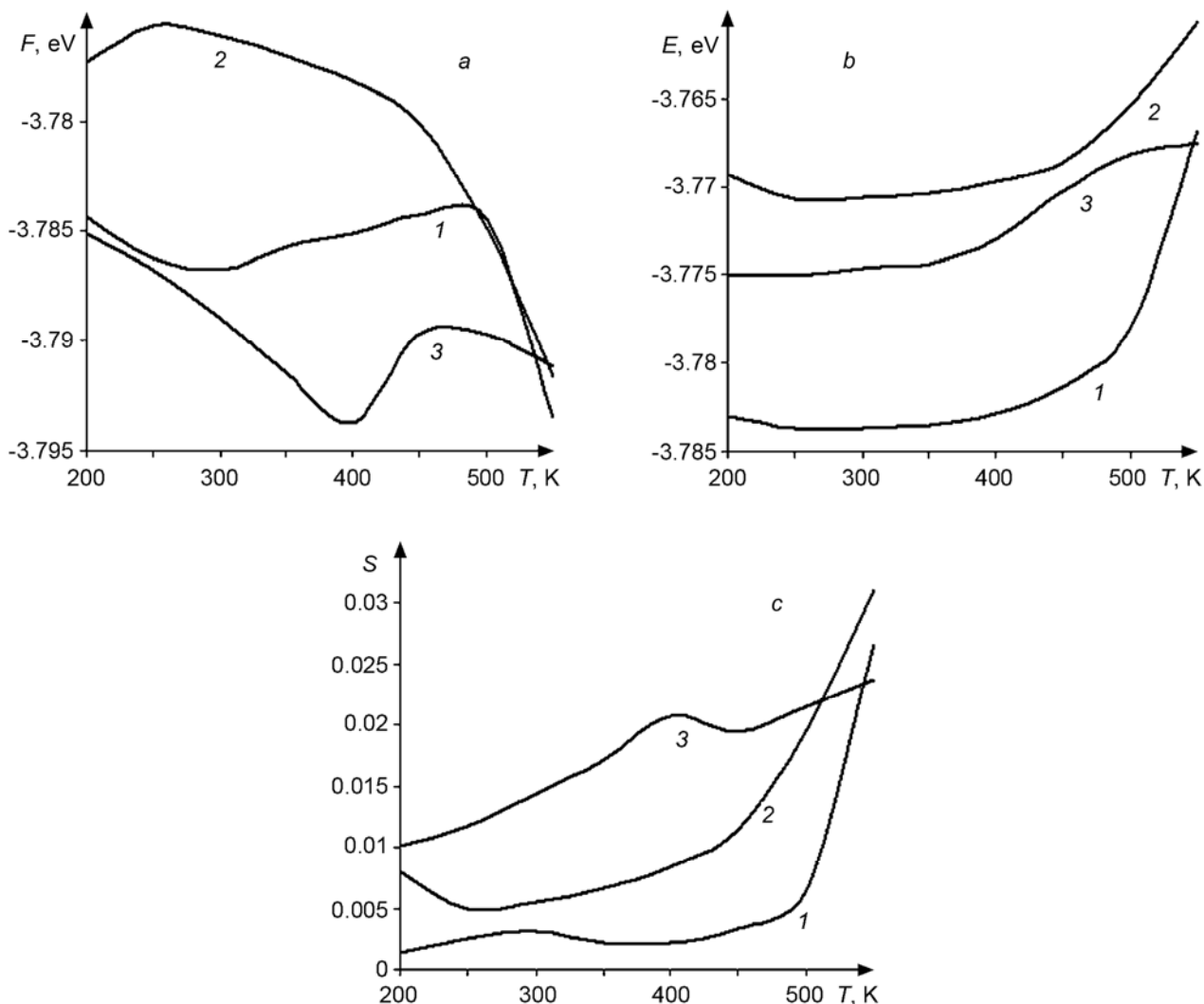


Fig. 2. Temperature dependence of free energy (a), configurational energy (b) and entropy (c) on the alloy component concentrations: 25 at.% Cu (curve 1), 30 at.% Cu (curve 2), and 20 at.% Cu (curve 3).

The behavior of the short-range order parameter in the first coordination sphere in the course of temperature variation (Fig. 1b) reveals that the alloy of stoichiometric composition shows that the most marked tendency to ordering (atoms tending to surround themselves by atoms of another kind) is manifested in the alloys of stoichiometric composition (curve 1), while in the case of deviation from stoichiometry towards a higher copper concentration (curve 2) this tendency is less conspicuous; and when the copper content is reduced there is a tendency to disordering (curve 3).

The energy characteristics included into the simulation of structural phase transition are free energy and its components: configurational energy and entropy. Shown in Fig. 2 are the calculated temperature dependences of free energy (Fig. 2a), configurational energy (Fig. 2b) and entropy (Fig. 2c).

The alloy of stoichiometric composition has the lowest value of configurational energy (Fig. 2a) and entropy (Fig. 2b) within the entire temperature range, with a sharp increase in the energy and entropy values at the temperatures higher than  $T=500$  K, which corresponds to the free energy maximum at  $T \approx 500$  K. It follows from the results obtained (Fig. 2) that there no transition heat, since, according to the Gorskii–Brag–Williams theory of ordering, in the

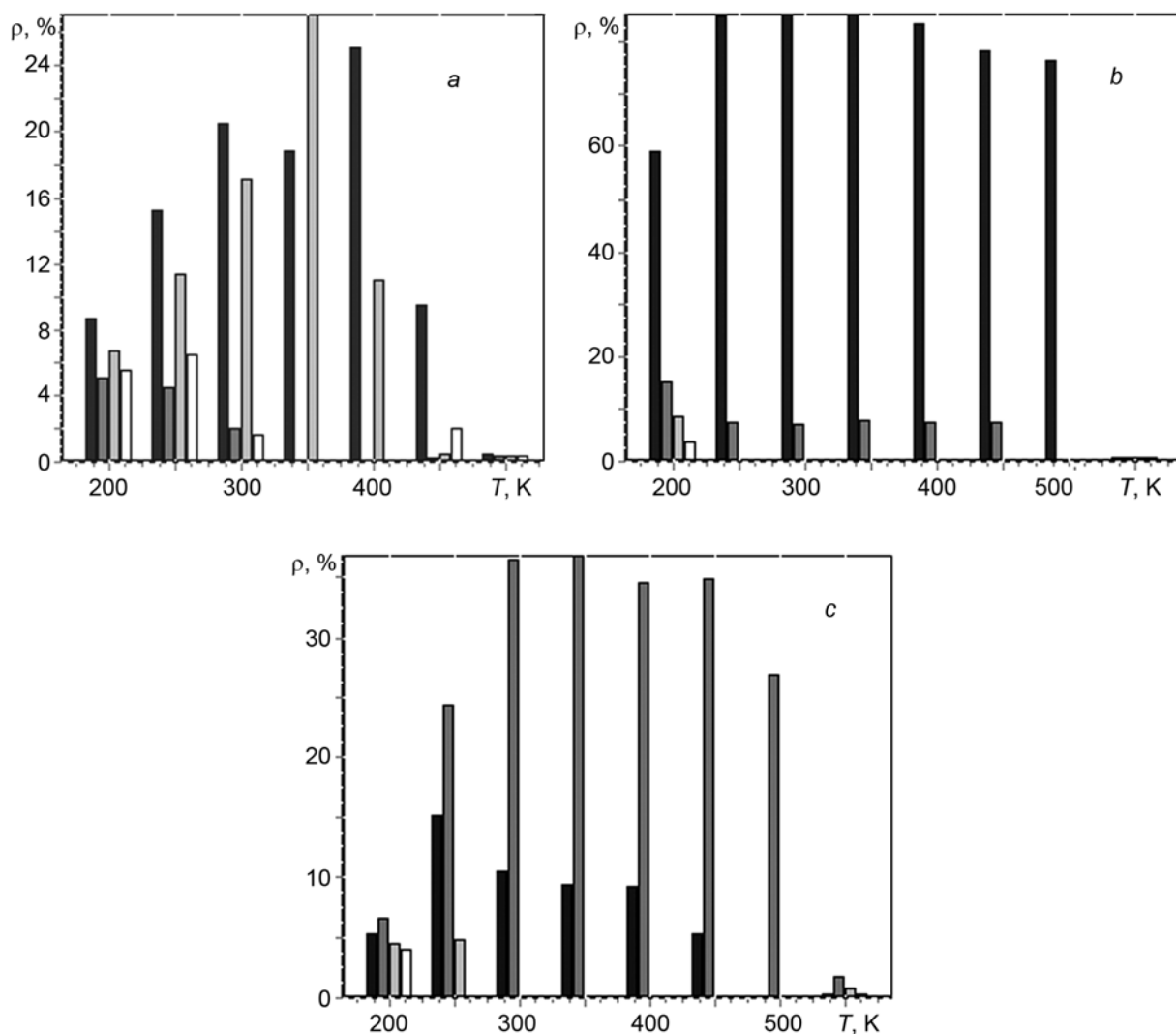


Fig. 3. Distribution of atoms over domains as a function of temperature in the alloy with the concentration of copper: 20 (a), 25 (b) and 30 at.% Cu (c). Antiphase domains are shown in different shades of gray.

alloy with 30 at.% copper the entropy in the course of a phase transition changes continuously. This, in turn, implies that the order–disorder phase transition in the alloy with 30 at.% copper is a transition of the second kind or close to it. In the alloys with 20 and 25 at.% copper the characteristics were observed to change abruptly, implying that the respective transitions were of the first kind.

**Peculiarities of domain structure in Cu–Au alloys in the alloy compositions close to that of CuAu<sub>3</sub> during thermoactivation.** Distribution of atoms over four antiphase domains is presented in Fig. 3.

The calculated diagrams show that the most highly ordered state is observed in the alloy of stoichiometric composition (Fig. 3b), in which within the temperature range 200–350 K the fraction of atoms belonging to the antiphase domains reaches 95%. It is readily seen from Fig. 3 that at the temperature ~200 K all types of antiphase domains are formed, with one of them predominating (up to 60% of the total number of atoms in the crystal). The fraction of atoms belonging to other domains is as low as 15%; as concerns their size they can be termed as microdomains. In the temperature range 250–350 K only two domains in the ratio 90 to 10% persist, which have an antiphase boundary in between. As the temperature increases to 400–450 K, the larger domain is smeared to 75%, and

at the temperature 500 K – the smaller domain is observed to annihilate completely. With the temperature increasing to 550 K, the alloy transits into a completely disordered state, all of the domains annihilating.

In the alloy with a lower copper content (20 at.% Cu) all types of domains are observed to form until the temperature reaches 300 K, while at an elevated copper concentration (30 at.% Cu) this takes place up to 250 K. For the case of 20 at.% copper, two types of domains are formed within the temperature range 350–450 K, and the total fraction of atoms belonging to the domains is reduced from 46 to 15%. For the case of 30 at.% copper, two types of domains are seen to predominate at the temperature from 300 to 450 K, and the total fraction of atoms decreases from 47 to 40%. In all the cases where the temperature is increased to 550 K the domains are observed to destroy and disordering of the alloy is accelerated.

It should be noted that the domain structure changes possess the following peculiarities. The principal mechanism of structural transformations in the early stage of the process of ordering is formation of antiphase domains [10–21]. In the course of simulation, all four types of domains are formed from the initial disordered state at the temperature ~200 K in all the cases under study.

In the alloy with the copper concentration 20 at.%, the first domain contains 8%, the second – 5%, the third – 7%, and the fourth – 6% of the total number of atoms. As the temperature is increased, larger domains increase in size and smaller domains annihilate. At the temperature  $T = 300$  K the first domain contains already 21%, the second – 2%, the third – 17%, and the fourth – 1% of the total number of atoms. At the temperature 350–400 K two antiphase domains are seen, which fluctuate with respect to each other, with the range of fluctuation corresponding to the extreme points of free energy. As the temperature is increased to 450 K, the process of disordering starts. Smaller domains are the first to smear, the fraction of larger domains is decreased, and antiphase microdomains are formed. At  $T = 500$  K we observe a completely disordered state.

In the alloy of stoichiometric composition at  $T = 200$  K the principal domain accounts for 60% and the second – 16%. In the range 250–450 K the ratio of the two domains is maintained the same, but when the temperature increases to  $T \approx 500$  K the second domain annihilates and the fraction of the first domain decreases down to 85%. At  $T \approx 550$  K the alloy is disordered.

In the case of the alloy with an elevated copper content (30 at.% Cu) the domain structure in the range 300–450 K is similar to that in the alloy of stoichiometric composition: there are two different size domains (40% in the first domain and 10% in the second). As the temperature is increased, the fraction of the smaller domain is decreased and at  $T = 500$  K is smeared entirely. At  $T = 550$  K, the alloy is entirely disordered. Compared to the alloy of stoichiometric composition, however, the maximum number of atoms belonging to the principal domain is as low as 40%, while in the case of stoichiometric composition it is as high as 90%.

**Peculiarities of disordered phase variations in the alloy compositions close to that of  $\text{CuAu}_3$  during thermoactivation.** Important elements of the disordering mechanisms are migrations, formation and faceting of antiphase and phase boundaries [22–25]. Peculiarities of structural composition of the disordered phase in the alloys with different concentrations of components are depicted in Fig. 4. Distribution of atoms over the clusters of the disordered phase in the case of copper concentration 20 at.% Cu (Fig. 4a) shows the minimum number of atoms belonging to the clusters, i.e., at the temperature below 400 K they account for approximately 40% of the total number of atoms, which increases up to 90% when the temperature is increased to 550 K.

Worth noting is the mechanism of variations in the disordered phase of the alloy, where the fraction of atoms belonging to the clusters and boundaries is associated with the presence of a disordered phase and a phase boundary. At an elevated copper concentration (30 at.% Cu) and stoichiometric composition (Fig. 4b and c) the fraction of clusters is negligible, while with the temperature increasing to  $T = 550$  K it reaches ~80%. The fraction of atoms belonging to the antiphase boundaries is the largest for the alloy with 30 at.% Cu within the entire temperature range from 200 to 500 K, which is indicative of a small-domain structure of this alloy. In the alloy of stoichiometric composition for the temperature increasing to 500 K there is a small increase in the fraction of atoms belonging to the antiphase boundary (up to 20%). This mechanism (when the fraction of atoms belonging to the antiphase boundary is increasing and the fraction of clusters is negligible) is primarily associated with fluctuation of antiphase domains and increased area of antiphase boundaries as a result of their faceting.

**Composition of structural elements in Cu–Au alloys in the alloy compositions close to that of  $\text{CuAu}_3$  during thermoactivation.** Investigations of structural states included the following phase compositions:  $A_3B$ ,  $AB$ ,  $AB_3$ ,

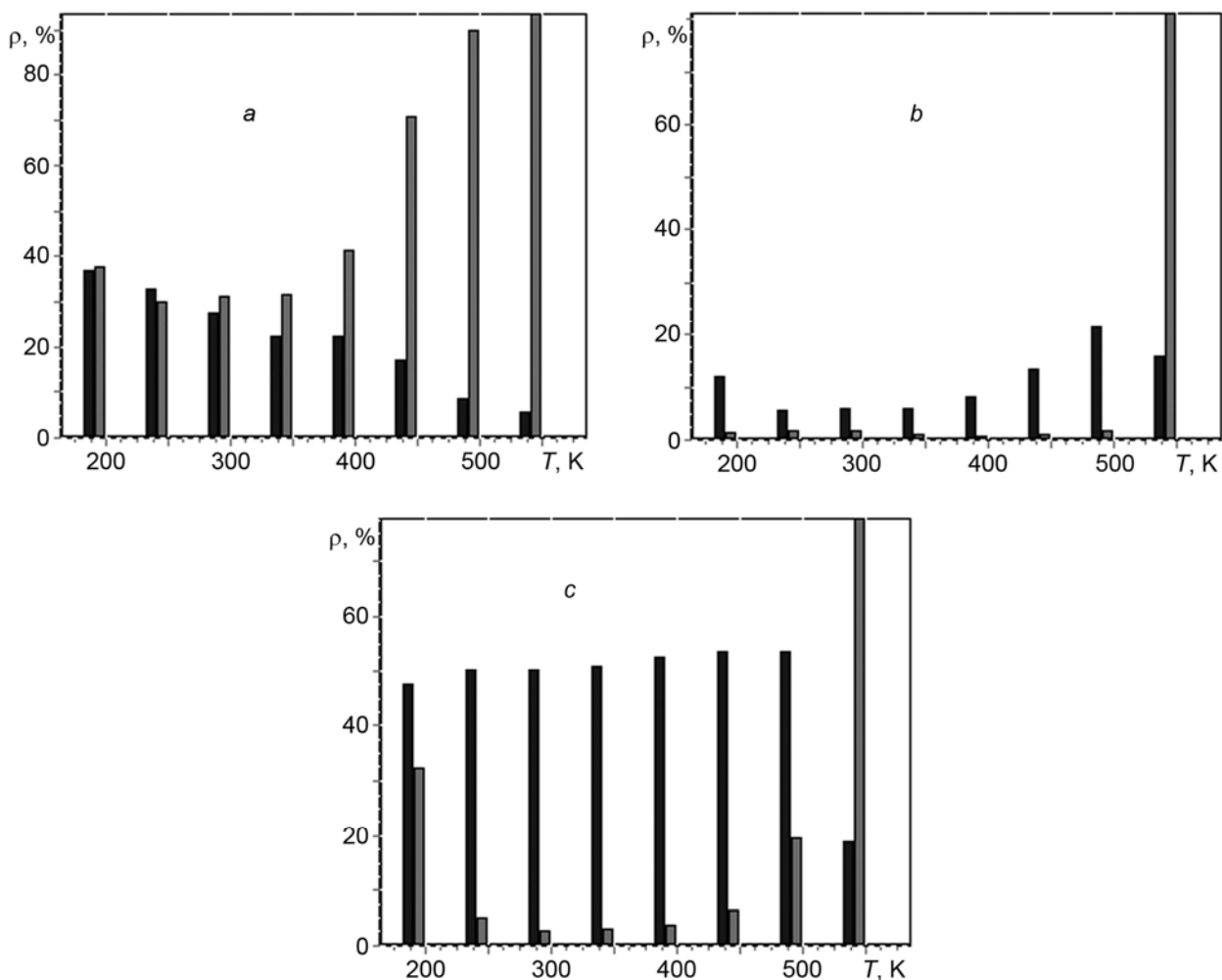


Fig. 4. Distribution of atoms over antiphase boundaries and clusters as a function of temperature in the alloy with: 20 (a), 25 (b), and 30 at.% Cu (c). Dark and light shades show the fractions of the antiphase boundary and clusters, respectively.

and pure components *A* and *B*. Figure 5 presents the distribution bar charts for the total phase fraction of superstructure  $L1_2$ . The formation of  $AB$  and  $AB_3$  phases is evident.

For the alloy of stoichiometric composition (Fig. 5b), the  $AB_3$  phase fraction is the largest, at the temperatures 200–250 K it is increased to 90%, then stabilized (to 400 K), and again reduced to 35% as the temperature approaches that of disordering. In this alloy, in addition to the  $AB_3$  phase (~90%), an  $AB$  phase was observed and that of a pure *B* component, their fraction being as low as 1%, though.

For the alloy with 30 at.% Cu (Fig. 5c) the fraction of the  $AB_3$  phase reaches a maximum in the distribution (~45%) in the temperature range 300–350 K, and at the temperature above 450 K one observes precipitates of the  $AB$  phase (up to 5%) and pure Au (on the order of 0.01%).

For 20 at.% Cu (Fig. 5a), the fraction of the  $AB_3$  phase in the distribution reaches its maximum (~45%) within the temperature range 250–350 K, the phase of pure Au is ~2%, and that of CuAu – less than 0.6%.

Thus it is clear that in the alloys of stoichiometric composition the fraction of atoms corresponding to the structural  $AB_3$  phase is limited to 44%, and the remainder of the crystal is said to belong to the disordered phase.

**Variations in size, shape and location of ordered and disordered phases in the  $\text{CuAu}_3$  alloy crystals during thermoactivation.** Shown in Figs. 6 and 7 are the structural elements of ordered and disordered phases in the



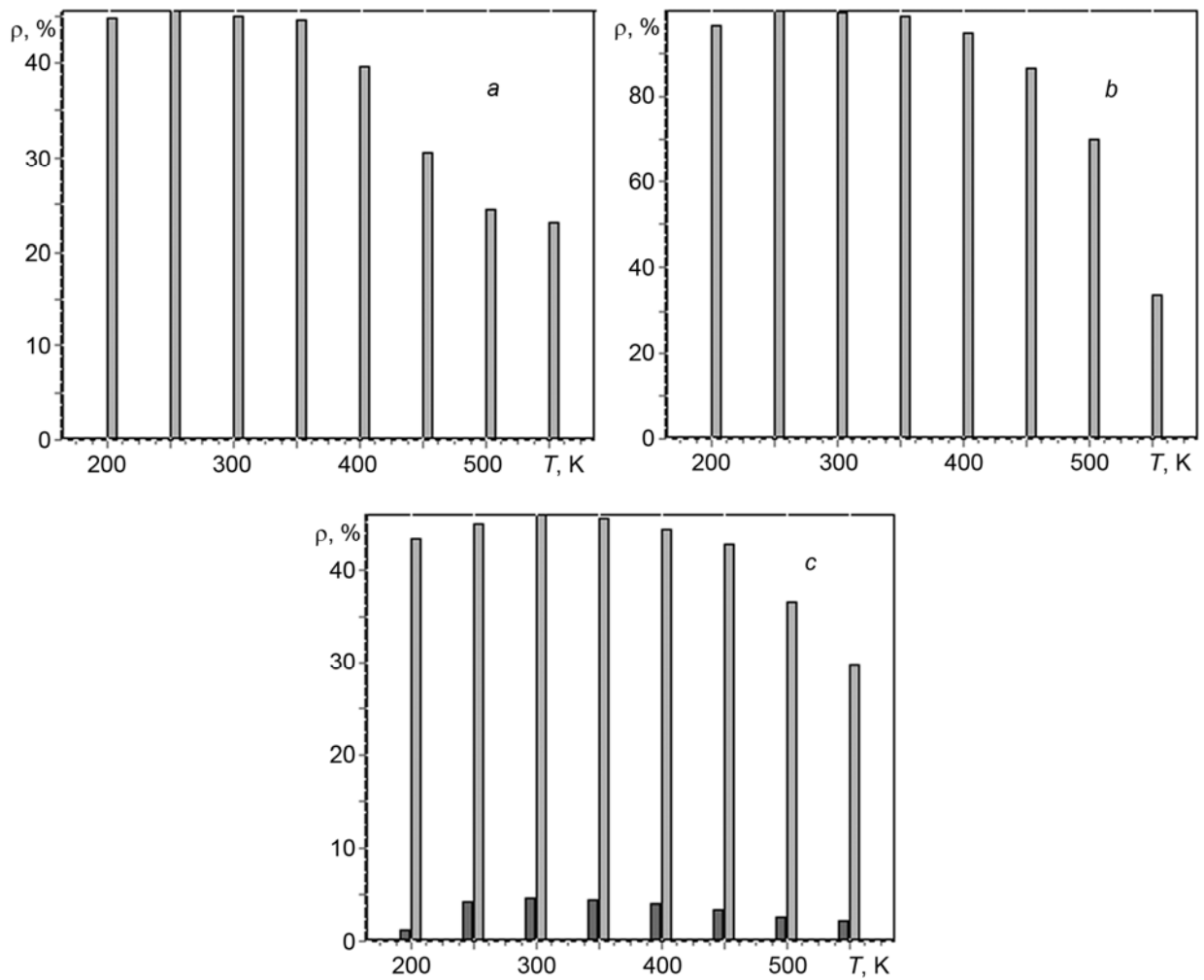


Fig. 5. Distribution of  $AB_3$  and  $AB$  phases as a function of temperature in the alloy with: 20 (a), 25 (b), and 30 at.% Cu (c). Dark and light shades show the structures  $CuAu_3$  and  $CuAu$ , respectively.

temperature interval from 200 to 550 K for the case of their outcropping to the surface of the 3D computation grid of the crystal under study. Different shades of gray indicate clusters, substitution point defects and their complexes, boundary atoms, and disordered and ordered regions. The highest ordering is achieved in the case of stoichiometric composition of the alloy at the temperatures 250–350 K.

In the alloy of stoichiometric composition, the long-range order parameter has the largest value 0.98, the total fraction of atoms belonging to the domains is maximal and is found to be 95%, and the value of the short-range order parameter persists to be negative up to the temperature 500 K (i.e., the alloy tends to atomic disordering in the entire temperature range investigated). At the temperature 250 K (Fig. 6a), one monodomain is observed to predominate along with three other smaller antidomains. The antiphase boundaries exhibit flattened structure, they lie in the  $\{100\}$  planes and separate the ordered phases.

At the temperature 300 K (Fig. 6b), the alloy exhibits the most ordered structure made up by two antiphase domains adjacent to each other. At 450 K (Fig 6c), a large number of point defects and their complexes are observed to form both at the antiphase boundary and in the bulk of the crystal. As the temperature increases to 500 K the antiphase domain is smeared.

In the alloy with 30 at.% Cu, the long-range order parameter has the largest value 0.87, the maximum total fraction of atoms belonging to the domains is 47%, and the value of the short-range order parameter remains to be

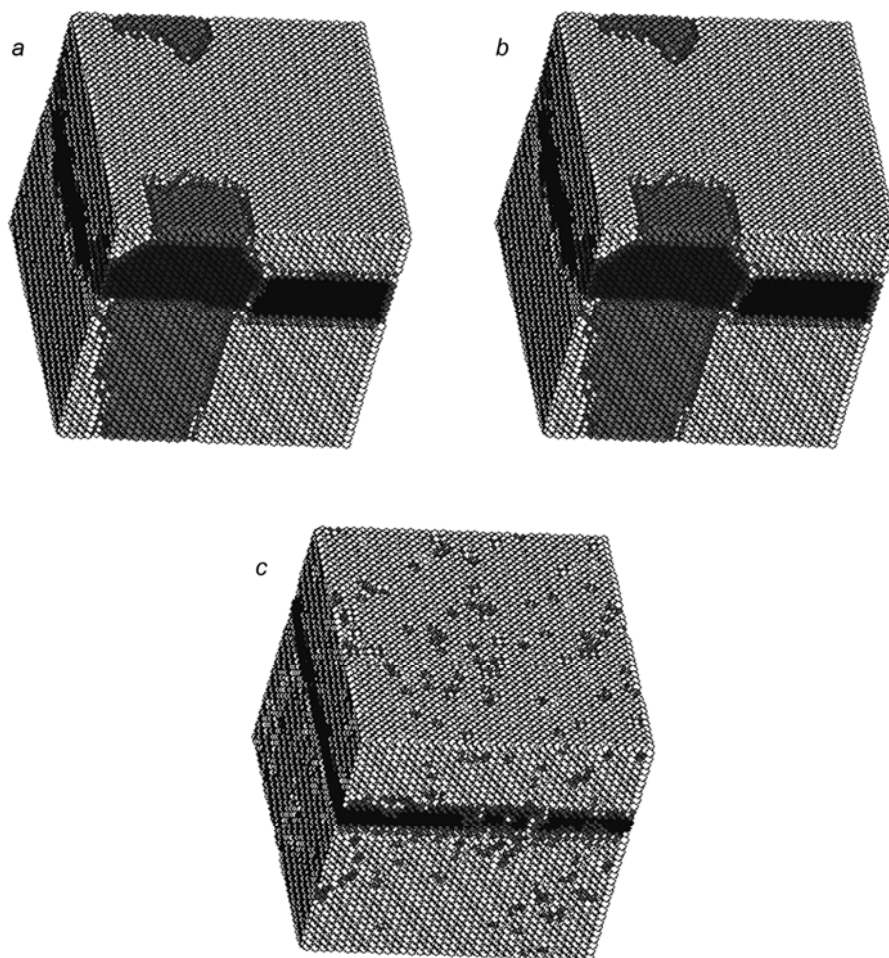


Fig. 6. Structure element distribution in the ordered and disordered phases in the alloy with: 25 at.% Cu and 75 at.% Al. Black shade shows the ordered phase, gray – disordered phase, other shades show antiphase microdomains at: 250 (a), 300 (b), and 450 K (c).

negative up to the temperature 500 K (similar to the stoichiometric case). At the temperature 200 K (Fig. 7a), there is predominance of small antiphase domains (microdomains) of different types.

The antiphase boundaries exhibit labyrinth structure and separate the ordered phases containing ~50% atoms. An increase in the temperature to 300 K (Fig. 7b) results in a most ordered structure that is made up of two antiphase domains adjacent to each other, note that they have resulted from merging and agglomeration of microdomains. At 450 K (Fig. 7c), the boundaries of the larger domain are observed to migrate and a large number of point defects and their complexes are formed at the antiphase boundary and in the bulk of the crystal. Disruption of the domain continuity provides an additional degree of freedom in the semi-ordered phase represented by thickened antiphase boundaries. As the temperature is increased to 500 K (Fig. 7d), the antiphase domain is smeared as a result of annihilation and the presence of a semi-ordered phase and clusters give rise to disordering of the crystal.

In the crystal with a lower concentration of copper (20 at.% Cu) there is predominance of the disordered phase. Medium-sized domains migrate and fluctuate and are smeared at higher temperature. The maximum fraction of atoms belonging to the antiphase boundary is 37%. At the temperature 250 K (Fig. 8a), there is a large number of small and medium-sized antiphase domains, and as the temperature rises to 300 K (Fig. 8b), two domains predominate and increase in their size. At the temperature 400 K (Fig. 8c) substitution point defects and small disordered phase spots are

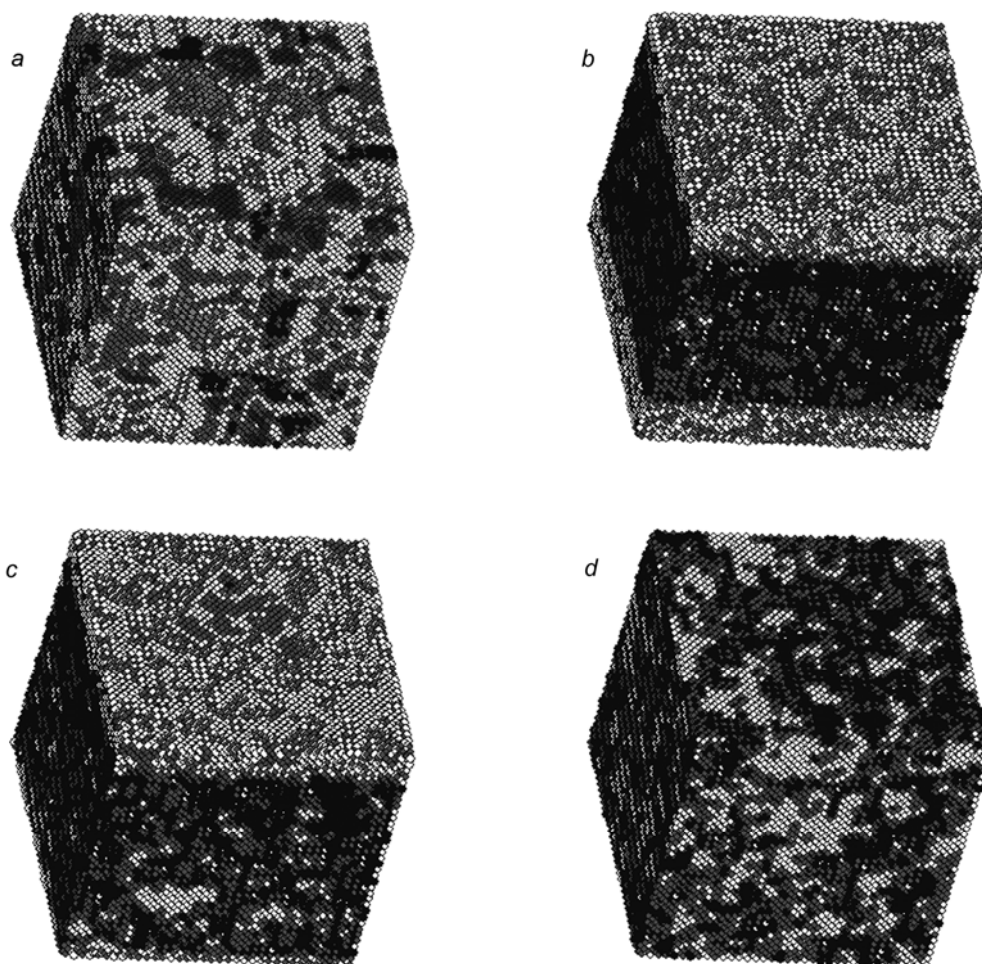


Fig. 7. Structure element distribution in the ordered and disordered phases of the alloy with 30 at.% Cu. Black shade shows the ordered phase, gray – disordered phase, other shades show antiphase microdomains at: 200 (*a*), 300 (*b*), 450 (*c*), and 500 K (*d*).

formed in the region of domains. With a further increase in the temperature, the domains are reduced in size and dissolved within the disordered phase. The long-range order parameter has the largest value 0.6, the maximum fraction of atoms belonging to the domains is 46%, and the short-range order parameter has positive values (i.e., there is no tendency to ordering).

Figures 6–8 depict distribution of the ordered (containing antiphase domains and microdomains) and disordered (containing clusters, substitution point defects and their complexes) phases. The most highly ordered states have been achieved by thermoactivation of the alloys: of stoichiometric composition at  $T = 300$  K (Fig. 6*b*), with an elevated copper content (30 at.% Cu) at  $T = 300$  K (Fig. 7*b*), and with a lower copper content (20 at.% Cu) at  $T = 250$  K (Fig. 8*a*).

**Principal mechanisms of ordering in Cu–Au alloys in the alloy compositions close to that of  $\text{CuAu}_3$  during thermoactivation.** An analysis shows that variations in the alloy composition result in different mechanisms of ordering and different conditions of the order – disorder phase transition.

Let us look at the mechanisms of structural transformations in the alloy of stoichiometric composition. At the temperatures below  $T = 350$  K, the disordered phase is rearranged into a microdomain structure, which is accompanied by formation of microdomains separated by antiphase boundaries. It is the phase boundaries that begin to play

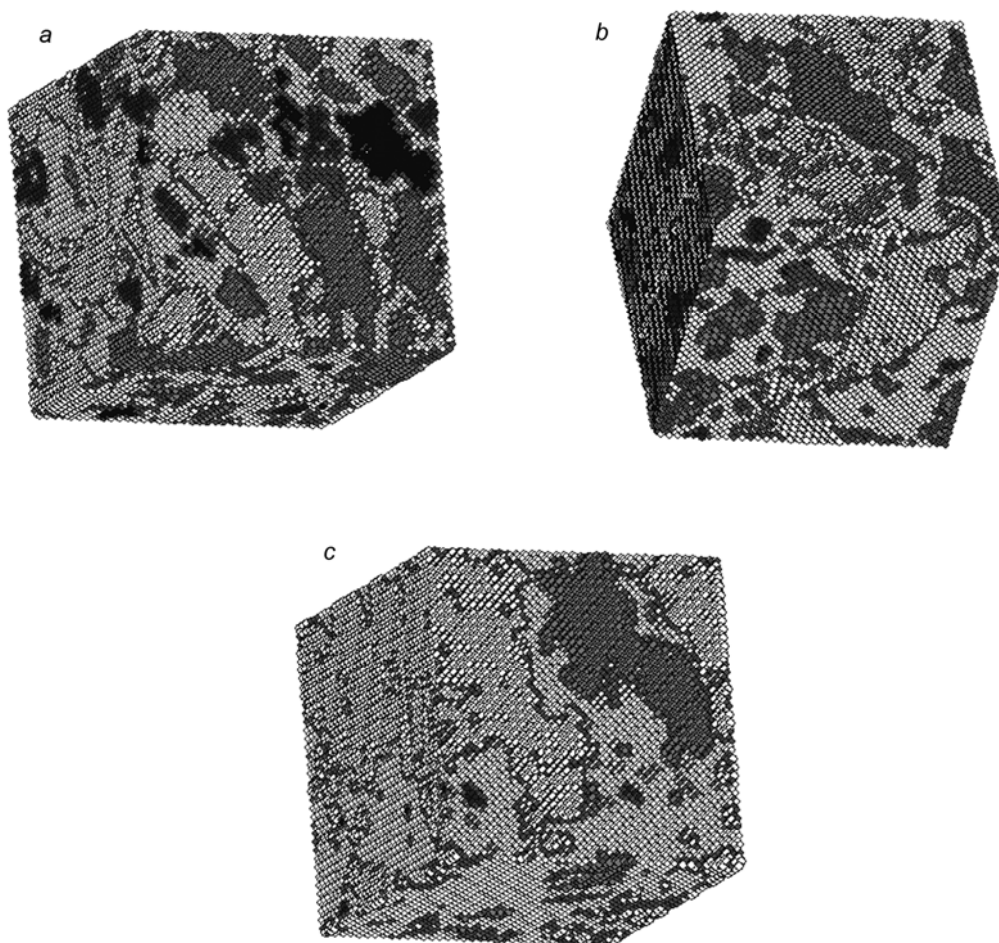


Fig. 8. Structure element distribution in the ordered and disordered phases as a function of temperature in the alloy with 20 at.% Cu. Black shade shows the ordered phase, gray – disordered phase, other shades show antiphase microdomains at: 250 (*a*), 300 (*b*), and 400 K (*c*).

an important role in ordering. We might assume that motion of the antiphase boundary is similar to that of dislocations, which takes place when vacancies are emitted and absorbed, since the antiphase boundary motion is realized by “emission and absorption” of substitution point defects. Note that formation of point defects along the antiphase boundaries of one of the domains indicates a regular atomic arrangement in the adjacent domain. In so doing, the antiphase boundary thickness does not change; it simply migrates across the crystal. Another feature of the boundary migration is flattening of the antiphase boundaries, which results in reduction of their area. The domains tend to become larger, with the microdomains and small and medium-sized domains annihilating. There is no domain migration, the structure is transformed mainly due to the motion of antiphase boundaries. Peculiarities of disordering also result in formation of segregations and clusters at the antiphase boundaries. Within the domains themselves, singular substitution point defects and their complexes are formed.

In the alloy with an elevated copper content (30 at.% Cu) the fraction of clusters is as low as 5% in the ordered state, while the fraction of the semi-ordered phase represented by phase boundaries is ~50%. In this alloy there is no domain migration, they increase in size mainly due to addition of atoms from the semi-ordered phase, i.e., phase boundary between the domains. Interaction between two adjacent domains occurs via their phase boundary that is comparatively thick and is further rearranged into one of the antiphase domains. The resulting domains have a high

density of substitution point defects and large areas of the ordered phase. In the course of ordering at low temperatures the semi-ordered region undergoes a comparatively fast rearrangement into a homogenous ordered phase, and in the course of disordering this semi-ordered region is rearranged into a disordered phase.

In the alloy with a lower copper content (20 at.% Cu), when in the most highly ordered state the disordered phase accounts for ~50%, the domains begin to migrate. They increase in size due to their coalescence accompanied by rearrangement of the smaller domain to fit the orientation of the larger one. Interaction of the domains occurs at the phase boundary between the ordered and disordered phase, with their shape, structure and size changing comparatively quickly. The phase boundary exhibits a labyrinth structure and in the course of disordering and increasing temperature intrudes into the ordered region.

## SUMMARY

The investigations performed in this study have demonstrated the efficiency of the proposed vacancy-based diffusion model of structural rearrangement of the ordering condensed state systems having both cubic and tetragonal or orthorhombic lattice in the ordered state.

Primarily, we have managed to follow in detail the pattern of ordering in binary Cu–Au alloys with a composition close to that of  $\text{CuAu}_3$  during thermal activation as a function of temperature and composition. Moreover, this process has been considered at the micro-, meso-, and macrolevel.

We have established that the phase transition in the alloys of stoichiometric composition (25 at.% Cu) and those with a lower concentration of copper (20 at.% Cu) is of the first kind, which is evidenced by abrupt changes in free energy. The situation is, however, qualitatively different in the alloy with a higher content of copper (30 at.% Cu), in which free energy of the system changes gradually without points of extremum, which suggests that the order – disorder phase transition in this model alloy is a transition of the second kind or close to it.

In the case of the alloy of stoichiometric composition, the long-range order parameter is close to unity up to the order – disorder phase transition temperature (~500 K). In the alloys with deviation from stoichiometry, the value of the long-range order parameter is naturally lower, the lowest value being observed in the alloy with a lower copper content.

In the alloys of stoichiometric composition and elevated copper content, the value of the short-range order parameter is negative up to the temperature 550 K, i.e., there are predominating tendencies to atomic ordering in this alloy within the entire temperature range of persisting ordered state, while in the alloy with a lower copper content no such tendencies are observed.

The principal mechanism of ordering in the early stage is formation of antiphase domains. In the model calculation, from the initial disordered state at the temperature 200 K four types of domains are formed. It should be noted that in the alloys with deviation from stoichiometry by 5 at.% the maximum fraction of atoms belonging to the domains is below 50% of their total number, while in the case of stoichiometry this fraction is 90%.

The investigation of structural state of the phase compositions ( $A_3B$ ,  $AB$ ,  $AB_3$ , and pure components  $A$  and  $B$ ) has shown that in the alloy of stoichiometric composition the fraction of atoms belonging to the phase  $\text{CuAu}_3$  is the largest and is found to be as large as 90% of the total number of atoms. In the alloys with deviation from stoichiometry, this fraction is below 45%, with the remainder defined as belonging to the disordered phase. Furthermore, in the alloy of stoichiometric composition we have also observed the phases of  $\text{CuAu}$  and pure Au; their fraction, however, was below 1% of the total number of atoms. In the binary alloy with 30 at.% Cu similar precipitates are the following phases:  $\text{CuAu}$  – up to 5%, pure Au – about 0.01% (at the temperature above 450 K), and in the alloy with 20 at.% Cu – the phases  $\text{CuAu}$  – less than 0.6% and pure Au – about 2%.

The mechanism of structural rearrangements substantially depends on peculiarities of mesostructure (domain structure, shape and size of domains, length and thickness of antiphase and phase boundaries, etc.). In the alloy of stoichiometric composition the fraction of clusters is small and the main role belongs to the mechanisms of faceting of antiphase boundaries, formation of microstructure segregations resulting in a lower intradomain ordering. The mechanism of structural rearrangements is primarily associated with smearing of the domain structures of the disordered phase.

We have revealed special features of migration of antiphase and phase boundaries in the structure: the boundaries are nonmobile and flattened. The process of disordering occurs both due to thickening of antiphase boundaries and lowering of the long-range intradomain order.

Among the important components of the mechanism of structural rearrangements are migration, formation and faceting of antiphase and phase boundaries. In the alloys of stoichiometric composition and those with elevated copper content (30 at.% Cu), the fraction of clusters is negligible. On the other hand, in the alloy with 30 at.% Cu the fraction of atoms belonging to phase boundaries turns out to be the largest ~50%, which testifies of either absence of homogeneity in the domain region or fine domain structure of this alloy.

In the alloy of stoichiometric composition, there are small fractions of atoms belonging both to the antiphase boundary and clusters. In this case, the mechanism of structural transformations is associated primarily with fluctuation of antiphase domain boundaries and increased area of the antiphase boundary due to its faceting.

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