

## LOW-STABILITY PRE-TRANSITIONAL STATES, ORDER-DISORDER PHASE TRANSITIONS, AND B2–A1 STRUCTURE TRANSFORMATIONS IN THE Cu – 40 AT.% Pd ALLOYS

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UDC 539.26+669.234

*Low-stability states and peculiarities of structural changes in the region of phase transitions are investigated using the Cu–Pd ~40 at.% Pd alloys as an example. To this end, the crystal lattice and long-range atomic order parameters and the Debye-Waller factors were determined in situ directly in the temperature range of the B2–A1 phases and the order – disorder phase transition using X-ray structural analysis. Based on the data obtained, peculiarities of the B2 and A1 phases in the CuPd alloys were analyzed near the structure-phase transitions and the behavior pattern of atomic vibrations in the crystal lattice was discussed. It is shown that in the CuPd alloys with ~40 at.% Pd, low-stability states are observed, which exhibit a number of anomalous phenomena (such as anisotropy of atomic displacements, splitting, heterophase fluctuations, nonlinearity of the lattice parameter and long-range order parameter dependences, etc.), which precede transformation of the alloy.*

**Keywords:** low-stability states, structure transformations, phase transitions.

### INTRODUCTION

Recently, a good deal of attention is given to low-stability states in condensed matter systems, which stems from peculiarities of their structure and promising application as functional materials [1–12]. However, only initial steps have been made so far to get an insight into the physics of formation of these states and their structural features. From our perspective, the Cu–Pd system is convenient to investigate: it has been studied for a comparatively long time with the numerous experimental data accumulated to date (e.g., [13–16]).

Considerable advances have been made by now in understanding the evolution of phase transitions in the alloys based on Cu–Pd (of particular interest is the composition near 40 at.% Pd) in the course of electron microscopy studies of their structure [17–20], X-ray diffraction studies *in situ* [21–24], and investigation of their physical properties [25, 26]. Despite these achievements, many features of structural changes in the region of phase transitions remain unclear.

Let us summarize the most important reliable experimental findings in these alloys.

First, the order – disorder phase transition (O-D PT) in these alloys is followed by the B2–A1 structural transformation (ordered bcc – disordered fcc). Second, the maximum of the hump in the phase diagram typical of the order – disorder PTs is accounted for the region with ~40 at.% Pd rather than that with the equiatomic composition [27]. Hence there is a question of the effect of nonstoichiometric composition on ordering during order – disorder PTs. Third, the state diagram according to [27] is conditionally equilibrium. In the CuPd alloys, an A1-phase can be formed in the low-temperature region by quenching from the temperatures higher than  $T_C$ . This indicates that the A1-phase is in a metastable state. On the other hand, deformation at room temperature initiates a B2→A1 PT, which testifies of the stability of the defect A1-phase and instability of the defect B2-phase at low temperatures [20, 24]. This is due to the

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nature of persistence of stable and metastable phases in the low-temperature region, where the thermoactivated processes hardly affect the structural-phase changes. Clearly, it is impossible to reach equilibrium states in the alloy. Fourth, in addition to the  $B2 \rightarrow A1$  PTs, the Cu–Pd alloys exhibit other peculiarities associated with extraordinary behavior of the crystal lattice both in the transition [21, 23] and pre-transition regions. The order – disorder PTs are controlled by the diffusion processes. The role of lattice instability in the latter case is absolutely vague. This supports the assumption that the  $B2 \rightarrow A1$  PTs in the CuPd alloys are complicated phenomena in their nature.

In this work we aim at clarifying certain features of structural changes in the region of phase transitions in the Cu–Pd alloys with ~40 at.% Pd.

## 1. MATERIALS AND EXPERIMENTAL PROCEDURE

The Cu – 39 at.% Pd and Cu – 36 at.% Pd alloys were smelted from high-conductivity copper and 99.99% pure palladium in an argon atmosphere. The melting was performed in a resistance furnace. For the X-ray diffraction studies use was made of both powder and bulk specimens. Disordered state was achieved by quenching from 800°C and ordered state – by lengthy annealing runs in a stepwise-cooling mode from 600 to 300°C with a step of 10°C per day. The high-temperature X-ray photography was performed in a GPVT-1500 chamber, with the temperature maintained accurate within  $\pm 2.5^\circ\text{C}$ . The measurements were carried out during isothermal exposure followed by a subsequent increase in the annealing temperature. The equilibrium state was determined from measurements of a number of parameters (the ratio of line strengths of the two phases, the ratio of the superstructure line strengths to the major line strengths, the angular position of the reflections and their half-widths) as a function of the exposure time at different temperatures.

## 2. PHASE TRANSITIONS $B2 \rightarrow A1$ AND $A1 \rightarrow B2$

### 2.1. Variation in structural-phase state during transitions

In the course of stepwise heating at the temperature 570°C, a  $B2 \rightarrow A1$  PT is being developed in the ordered Cu – 39.5 at.% Pd alloy (Fig. 1a, curve 1). As the temperature is further increased, disordering in the  $B2$ -phase occurs at 600°C only (Fig. 1a, curve 2).

Shown in Fig. 1b are the temperature dependences on the anomalous long-range order parameter and the  $B2$ -phase volume fraction during the reverse  $A1 \rightarrow B2$  transition. We have found out that the ordered phase with a  $B2$ -phase structure in this case is formed at 580°C. The degree of long-range atomic ordering in the  $B2$ -phase is increased abruptly within a narrow temperature interval ( $\sim 10^\circ\text{C}$ ) to the values as high as 0.8. A further decrease in the annealing temperature from 580°C does not yield any substantial increase in the order parameter, while the volume fraction of the ordered phase is monotonously increased with the decreasing temperature. The regions of persisting two phases,  $B2$  and  $A1$ , do not coincide, which indicates the presence of a hysteresis during the  $B2 \leftrightarrow A1$  transition and represents a real situation where transformation occurs under certain overcooling to the values below  $T_0$  (or overheating to the values above  $T_0$ ) necessary for a new phase to nucleate. An analysis of the variations in the  $B2$  volume fraction shows that the onset of the  $A1 \rightarrow B2$  transition coincides with that of the  $B2 \rightarrow A1$  transition (Fig. 1b).

In the CuPd alloy under study, the order – disorder PT is accompanied by a structural  $B2 \rightarrow A1$  phase transition. Comparing the plot of  $\eta = \eta(T)$  in the Cu – 39.5 at.% Pd alloy (Fig. 2) with the well-known dependences from the CuZn, FeCo and AgZn alloys [28], which undergo an order – disorder PT of the second-order ( $B2 \rightarrow A2$  PT) not complicated by structural transformations, we can readily conclude as follows. During heating, the temperature dependence of the long-range order parameter in the Cu – 39.5 at.% Pd alloy does not coincide with the plot  $\eta = \eta(T)$  for the alloys undergoing an order – disorder PT only and having a nearly stoichiometric  $AB$  composition. The temperature dependence of the atomic long-range order parameter in the phase with the  $B2$  structure of the alloy in question is much steeper compared to the same curves from the CuZn, FeCo and AgZn alloys (Fig. 2). On the one hand, these data indicate considerable differences in the processes of disordering in the  $B2$ -phase, taking place during the

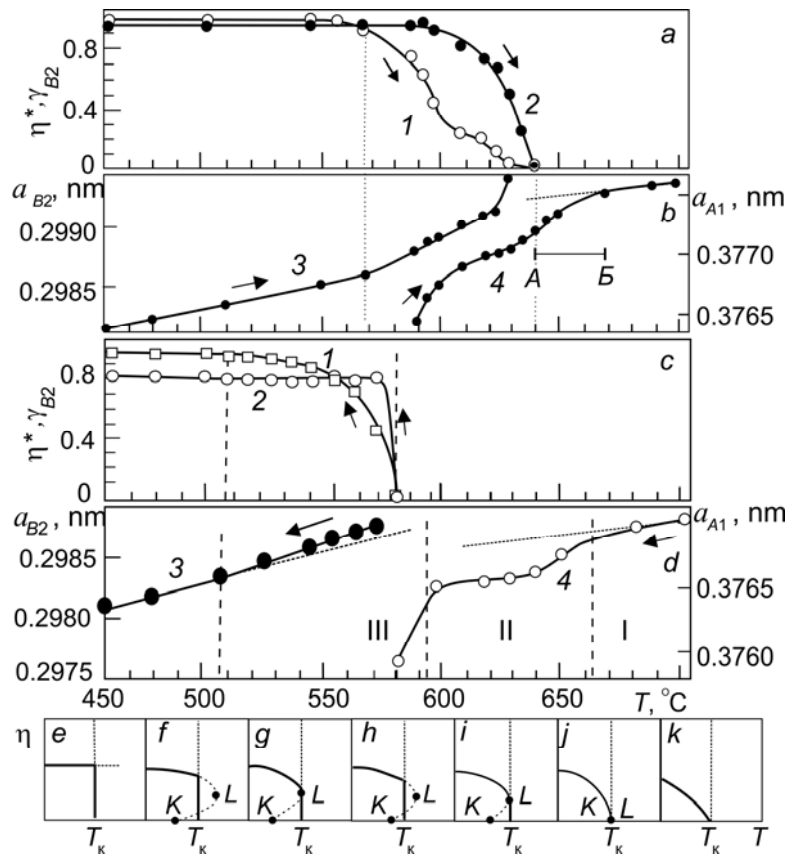


Fig. 1. Temperature dependences of the volume fraction of the  $B2$ -phase (curve 1), ordering degree in the  $B2$ -phase (curve 2), unit cell parameters in the  $B2$ - (curve 3) and  $A1$ -phases (curve 4) during the  $B2 \rightarrow A1$  (a, b) and  $A1 \rightarrow B2$  (c, d) PTs in the Cu – 39.5 at.% Pd alloy. The classification of PTs with respect to the long-range order parameter is as follows: first-order PT (e), first-order order – disorder PT (f), critical first-order disordering (g), critical first-order ordering (h), critical first-order PT (i), anomalous first-order PT (j), and second-order PT (k) [28].

order – disorder  $B2 \rightarrow A2$  phase transition and  $B2 \rightarrow A1$  structural transition. This is associated with the presence of two phases in the region of PT and adds the features of the first-order PT to this transition. On the other hand, variation in the order parameter in the  $B2$  superstructure within the temperature region close to  $T_C$  has its own peculiarities that characterize the order – disorder PT as one close to the second-order phase transition.

In [28] it was shown that in order to analyze an order – disorder PT, the commonly accepted PT classification according to Paul Ehrenfest [29], who identified first-order and second-order transitions only, has to be added with a more detailed data (Fig. 1e–j). From the considerations and data reported in [28] follows that the order – disorder PT complicated by a structural transition and the behavior of  $\eta = \eta(T)$  in the region of this PT should be analyzed using an extended classification.

During the direct and reverse order – disorder PTs the plots  $\eta = \eta(T)$  in the  $B2$ -phase are very different (Fig. 1a and b). During heating in the course of the  $B2 \rightarrow A1$  PT, disordering in the  $B2$ -phase occurs as a PT close to the second-order transition. According to the classification in [28],  $\eta = \eta(T)$  belongs to Type 6, and the PT is an anomalous first-order phase transition (Fig. 1a and g). During heating in the course of the  $A1 \rightarrow B2$  PT, however, order parameter  $\eta$  is abruptly increased in the  $B2$ -phase within a narrow temperature interval. This indicates this transformation to be a critical first-order ordering and, according to [34], it belongs to Type 4 (Fig. 1f). The differences in the transition types during ordering and disordering revealed in that work has provided the evidence that the mutual position of the stability limits in the ordered and disordered phases can result in different PTs. While in the case of an order – disorder PT not

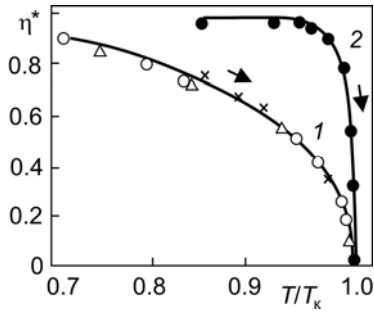


Fig. 2

Fig. 2. Behavior of the long-range order parameter in the  $B2$  superstructure (curve 1) during the order – disorder PT ( $B2-A2$ ) in the AgZn, FeCo, and CuZn alloys [28] and during the order – disorder PT ( $B2-A1$ ) in the Cu – 39.5 at.% Pd alloys (curve 2) versus the temperature used (o – AgZn,  $\times$  – FeCo, and  $\Delta$  – CuZn).

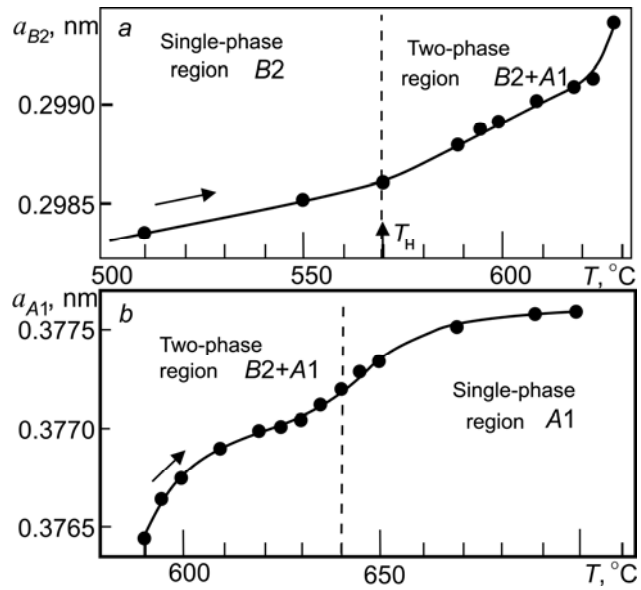


Fig. 3

Fig. 3. Temperature dependences of the lattice parameter in the  $B2$  (a) and  $A1$  (b) structures during heating from an ordered state under the condition of the  $B2-A1$ PT.

complicated by a structural transition no such difference was observed [28], it is possible when an order – disorder phase transition occurs together with a structural bcc – fcc PT. This allows us to assume that in this region of low-stability structural states, the direct and reverse  $B2 \leftrightarrow A1$  PTs would follow different mechanisms. Indeed, the presence of a hysteresis during the structural  $B2-A1$  PT cause the ordering and disordering processes to occur within different temperature intervals. Moreover the presence of a hysteresis changes the character of PTs in this region of low-stability structural states and, based on the experimental data, we can argue that disordering in the  $B2$ -phase is shifted into a different temperature interval due to the  $B2 \rightarrow A1$ PT.

## 2.2. Crystal lattice behavior during the $B2 \rightarrow A1$ phase transition

Shown in Fig. 3a is the temperature dependence of the lattice parameter of the  $B2$ -structure ordered phase obtained for the case of heating the Cu – 39.5 at.% Pd alloy from a completely ordered state. The dependence bears a linear character up to the starting PT temperature, with the inflection point observed in the plot at this temperature. It is clearly seen that there are no singularities in the lattice parameter behavior prior to the start of the transformation, likewise there are no Bragg reflections of the  $B2$  structure in the temperature dependences of the line strengths. Clearly, the temperature dependences of the thermal expansion coefficient in the phases with the  $B2$  and  $A1$  structures allow us to reveal singularities in the temperature dependences of the respective lattice parameters. In the cases where the lattice parameter vs. temperature curve is broken by a jog, the thermal expansion vs. temperature curve has a corresponding finite-value jog of coefficient  $\alpha$ . The stepwise increase in coefficient  $\alpha$  indicates that the crystal lattice of the  $B2$ -structure phase in this temperature interval has transferred into a new, low-stability (less stable) state with respect to that within the low-temperature interval. This testifies of the crystal lattice being prepared for a PT.

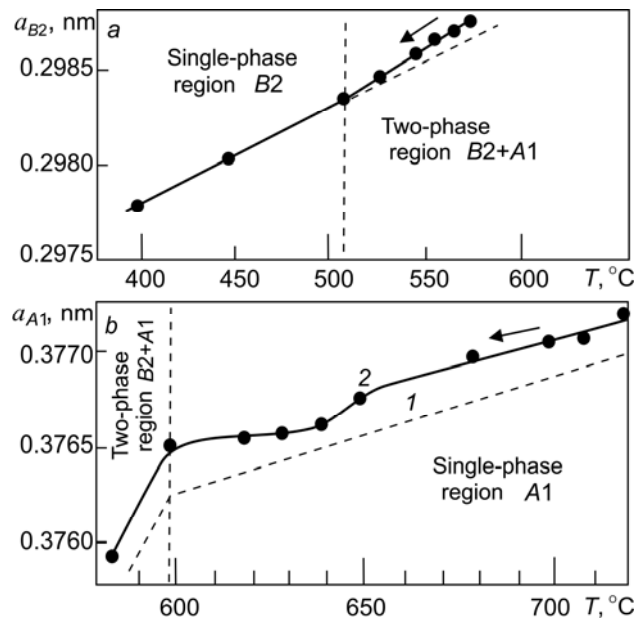


Fig. 4. Dependences of the lattice parameters in the  $B2$  (a) and  $A1$  structures (b): theoretical curve 1 and experimental curve 2 during cooling in the course of the  $A1$ – $B2$  PT.

The temperature dependence of the lattice parameter of the  $A1$ -structure high-temperature phase is given in Fig. 3b. In this temperature range upon completion of the  $B2$ → $A1$  transition, the dependence deviates from linearity.

An analysis of the temperature dependences of the structural line intensity logarithm allowed us to find out that when the temperature is increased from 25 to 570°C, which precedes the  $B2$ → $A1$ PT, there is a linear decrease in the Bragg reflection intensity of the ordered  $B2$ -phase. Using the Debye model we determined the Debye-Waller factor that is dependent on the temperature both far from the PT and close to it. From the temperature dependences of the integral intensity of the reflections and the Debye-Waller factor in the ordered phase, we found no signs of instability prior to the  $B2$ → $A1$  transition. This indicates that the phase is stable, even though this stability is very low. As the temperature is further increased, there is a  $B2$ → $A1$  PT via the two-phase region. An increased intensity of reflections from the  $A1$  structure in the two-phase region is due to an increased volume fraction of the  $A1$ -phase.

### 2.3. Crystal lattice behavior during the structural $A1$ → $B2$ phase transition

We have studied the variation in the lattice parameter of the phase with the  $A1$ -structure during slow cooling from a single-phase state (Fig. 3). An  $A1$ → $B2$  PT in this case begins at the temperature  $\sim 590$ °C. In the temperature dependence of the lattice parameter we can single out three sections. The first is the one far from the transition, and the curve is ordinary, i.e., it is linear. The second section is the temperature interval immediately before the  $A1$ → $B2$  transition, where the anomalous dependence on temperature is already observed. The third section is the temperature interval inside the  $A1$ → $B2$  PT, in which case the X-ray patterns contain reflections from the newly formed phase.

Let us address the lattice parameter variation of the ordered phase with the  $B2$  structure during cooling (Fig. 4a). The structural  $A1$ → $B2$  phase transition in this case is completed at the temperature 510°C. After it is over, the lattice parameter of the  $B2$ -phase is linearly decreased with the temperature, this behavior of the ordered-phase lattice parameter being observed prior to the  $B2$ → $A1$  transition (Fig. 3b).

Far from the temperature of the starting  $A1$ → $B2$  transition, the crystal lattice of the disordered solid solution is under an ordinary condition characterized by a linear dependence of the integral intensity of the reflections on the temperature. We have found out that in the temperature interval prior to the  $A1$ – $B2$  PT the intensity of the reflection from the  $A1$ -phase is anomalously high. The character of the temperature dependence of line strength (331) during

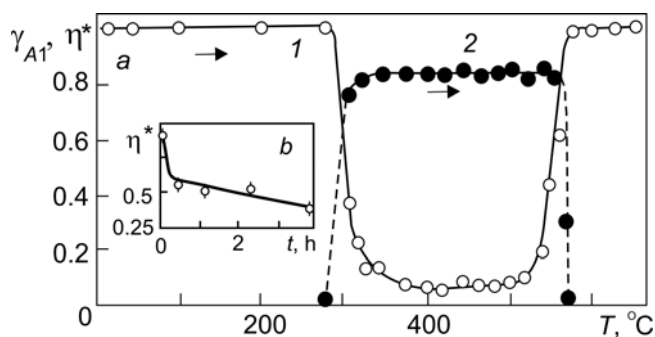


Fig. 5. Temperature dependence of the atomic fraction of the  $A1$ -phase ( $a$ , curve 1) and the long-range order parameter in the  $B2$ -phase ( $a$ , curve 2). The dependence of  $\eta^*$  in  $B2$  on the time of isothermal annealing at  $580^\circ\text{C}$  ( $b$ ).

cooling of the disordered specimen from high temperatures (Fig. 4b) is the same as it is during heating after the  $B2 \rightarrow A1$  PT (Fig. 4a), in other words at the temperature approaching that of the start of the transition, the dependences of the intensity of the reflections from the  $A1$ -phase are nonlinear. The temperature interval of the low-stability, pre-transitional state is somewhat displaced towards lower temperatures. The effect of the change in the intensity of reflections from the  $A1$ -phase prior to the transition is fully reversible. The weakly pronounced hysteresis of this phenomenon is likely to be due to that of the  $B2 \rightarrow A1$  transition.

To sum up, in the temperature range of low-stability states preceding the  $A1 \rightarrow B2$  PT, the crystal lattice of the  $A1$ -phase exhibits certain singularities represented as an unusual behavior of the parameters describing the crystal lattice state.

### 3. STRUCTURAL PHASE TRANSITIONS $A1_{\text{qu}} \rightarrow B2 + A1 \rightarrow A1$

#### 3.1. Variations in the structural phase state during PT

It has been established that during heating of the Cu – 36 at.% Pd alloy produced by quenching from the temperatures above  $T_C$ , the structural phase state changes:  $A1_{\text{qu}} \rightarrow A1 + B2 \rightarrow A1$  (Fig. 5a). Within the temperature interval  $300\text{--}600^\circ\text{C}$  in the  $A1$ -phase there is a significant phase concentration inhomogeneity, which is manifested in a conspicuous broadening of the reflections from the  $A1$ -phase. A decrease in the effective long-range order parameter  $\eta^*$  with time corresponds to the process of atomic disordering (Fig. 5b). The most intensive decrease in the values of  $\eta^*$  occurs at the initial point of time. Further annealing at this temperature hardly affects the order parameter value. This is the boundary-value temperature. As the temperature is increased by  $5^\circ\text{C}$ , the  $B2$ -structure phase is no longer observed. The ordered  $B2$ -phase disappears after a jog ( $\Delta\eta^* \sim 0.3$ ) of the order parameter.

#### 3.2. Peculiar crystal-lattice behavior in the phases under the $A1_{\text{qu}} \rightarrow B2 + A1 \rightarrow A1$ PT

Using the methods of X-ray diffraction, we examined the temperature dependences of the intensities of Bragg reflections from the  $A1$  structure during heating from the temperatures higher than  $T_C$ . This structure is in a metastable state. One cannot but notice the different behavior of line intensities of different reflections from the  $A1$ -phase as a function of temperature. The intensity of the (111) reflection is decreased prior to the PT within the temperature interval  $200\text{--}350^\circ\text{C}$ . For the (200), (220) and (331) reflections the dependence is maintained to be linear.

Using the X-ray diffraction methods, we managed to reveal certain singularities in the temperature dependences of the interference intensity maxima from the ordered phase with the  $A1$  structure both in the high- and low-temperature

regions prior to the PT. This provides evidence of an existence of a pronounced low-stability pre-transitional state in a disordered solid solution based on an fcc-lattice.

Pre-transitional phenomena and low-stability states were found and described in the alloys undergoing martensitic transformations (MTs) [2–7]. In the present work these phenomena and states are formed in the alloys based on Cu–Pd with a structural  $B2 \rightarrow A1$  transition taking place simultaneously with an order – disorder PT. On the whole, this indicates a great variety of pre-transitional phenomena and a universal character of low-stability states, as well as the presence of special features of structural-phase changes in each alloy prior to and during a PT.

Relying on the data obtained, we calculated the total number of the r.m.s. displacements of atoms from their equilibrium positions. In the disordered  $A1$ -phase stabilized by quenching, long before the start of a monotropic (irreversible) PT ( $\sim 150^\circ\text{C}$ ) there is an anomalous increase in the total values of the r.m.s. displacements of atoms from the average lattice of the disordered  $A1$ -phase. The anomalous variation in the r.m.s. displacements of atoms is also observed in the high-temperature interval of the phase with the  $A1$  structure after the  $B2 \rightarrow A1$  transition is completed. Upon completion of the PT, the total atomic displacements are decreased becoming even smaller than those prior to the transformation at  $300^\circ\text{C}$ . Later, their values exhibit a maximum and form a normal linear dependence.

This variation in the r.m.s. atomic displacements indicates a low-stability, pre-transitional state of the crystal lattice, which is attributed to its ‘softening’ before the transition. The measurements of the atomic displacements in the Cu and Pd sublattices in the  $B2$ -phase and in the  $B2+A1$  two-phase region demonstrate that in the copper sublattice the atoms in the ordered  $B2$ -phase possess higher values of atomic displacements than the average atomic displacements in the  $A1$ -phase, while those in the Pd sublattice have lower values.

Thus, the values of the completed r.m.s. atomic displacements in the disordered phase with the  $A1$  structure obtained from the experimental X-ray diffraction data on the intensities of Bragg reflections also allow us to reveal low-stability pre-transitional crystal-lattice states within the temperature intervals before the start of the monotropic  $A1_{\text{qu}} \rightarrow B2$  PT and after the  $B2 \rightarrow A1$  transition. The low-stability pre-transitional states in the low-temperature region considerably differ from those crystal-lattice states in the high-temperature region after the  $B2 \rightarrow A1$  PT is completed.

From the temperature dependence of the total number of r.m.s. atomic displacements in the disordered phase with the  $A1$  structure we isolated the contribution of the static r.m.s. displacements. The value of the latter atomic displacements was equal to  $(0.005 \pm 0.003)$  nm.

The r.m.s. displacements of atoms were evaluated in a solid solution of an fcc Cu – 36 at.% Pd alloy, whose value was found to be equal to 0.004 nm. These displacements in the disordered phase with the  $A1$  structure make but only a slight contribution into the total/complete r.m.s. displacements of atoms in the high-temperature region, the major contribution coming from the dynamic displacements of atoms. Note a very important fact: it is virtually impossible to differentiate between the static and dynamic contributions in the temperature curve prior to the transition into a low-stability state and in the region of the PT using X-ray diffraction method.

For the Cu – 40 at.% Pd alloys we calculated the lattice deformation during the bcc – fcc transition following the Bein scheme and its minimum and maximum values were found to be  $\sim 11\%$  and  $26\%$ , respectively. The minimum value of deformation during the bcc – fcc restructuring of the lattice according to this scheme is comparable with that of r.m.s. displacements of atoms. This circumstance allows us to assume that the homogenous Bein deformation along the  $\langle 110 \rangle_{\text{fcc}}$  direction is favorable for a transition into an fcc-lattice, which is not the case along the  $\langle 100 \rangle_{\text{fcc}}$  direction. The data obtained indicate that the fcc-bcc transition according to the Bein scheme via homogenous deformation is complicated. Other mechanisms might be more preferable. For instance, the rearrangement of fcc – bcc lattices can occur via generation of short-range order regions in the fcc – structure in its low-stability state by combining the displacement waves with a  $\mathbf{k} \parallel \langle 110 \rangle$  vector and the longitudinal wave along  $\langle 110 \rangle$ .

Thus, we have revealed an unusual low-stability state of the crystal lattice of the disordered  $A1$  phase prior to the PT both in the high-temperature equilibrium region of its persistence and in the low-temperature metastable region. This behavior of the atomic displacements in the  $A1$  phase can represent the development of heterophase fluctuations in the low-stability pre-transitional region.

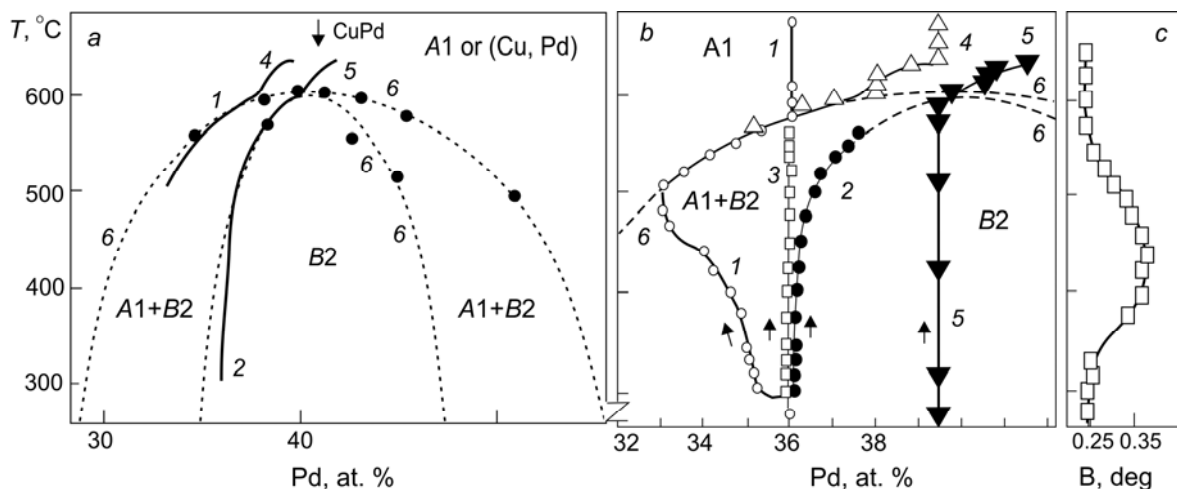


Fig. 6. Section of the DOS for the Cu – Pd alloys [27] (a) and the concentration dependence in the Cu–Pd alloys close to the 40 at.% Pd composition in the  $B2$  and  $A1$  phases (b) calculated from the temperature dependences of the lattice parameters in the  $A1$ - (curves 1 and 4) and  $B2$ -phases (curves 2 and 5). Curve 3 was constructed using the lever relation from curves 1 and 2; it characterizes the concentration composition in the alloy. Curve 6 was constructed using the data from [27]. The half width of the (111) Bragg reflection in the  $A1$ -phase (c) during heating of the hardened Cu – 36 at.% Pd alloy.

#### 4. CONCENTRATION INHOMOGENEITIES AND DELAMINATION IN THE CuPd ~ 40 AT.% Pd ALLOY

Based on the X-ray diffraction data on the phase composition and variation in the concentration of the co-existing phases in the two-phase region we constructed a section in the phase diagram of the Cu–Pd system close to 40 at.% Pd. The data on the concentration-induced variations in the phases were obtained from the experimental temperature dependences of unit cell parameters of  $A1$  and  $B2$  structures within the temperature range 20–700 $^{\circ}\text{C}$  and relying on the calculated dependences of these parameters on concentration in the Cu–Pd alloys [22].

Figure 6 illustrates the literature data on the section of the equilibrium DOS of the Cu–Pd system [27] (Fig. 6a) and the data obtained in the course of investigation of the structural-phase states in the Cu – 39.5 at.% Pd and Cu – 36 at.% Pd alloys [19].

Let us identify a few features of the structural-phase composition revealed during heating of the disordered Cu – 36 at.% Pd alloy, which are due to the  $A1_{\text{qu}} \rightarrow B2 \rightarrow A1$  PT (Fig. 6b, curve 1). It has been established that the half width of the reflections in the  $B2$ -phase hardly changes. It follows from the above that even though the ordered phase exhibits concentration inhomogeneity this inhomogeneity is negligibly small. In the disordered solid solution an equilibrium concentration can be achieved at the temperature 500 $^{\circ}\text{C}$  only, i.e., within the temperature interval from 300 to 500 $^{\circ}\text{C}$  the  $A1$  structure is non-equilibrium. Note that the  $A1$  structure also demonstrates very high concentration inhomogeneity expressed in broadening of the Bragg reflections with increased temperature (Fig. 6c). This concentration inhomogeneity considerably decreases once the system achieves an equilibrium state, which is consistent with the phase diagram (Fig. 6b).

The results of investigation of concentration variations in the disordered and ordered phases, obtained during heating of the ordered Cu – 39.5 at.% Pd alloy, are presented in Fig. 6b by curves 4 and 5, respectively. The two-phase region ( $A1+B2$ ) was established to be narrow, without any broadening of the Bragg reflections of  $A1$  and  $B2$  phases, which is indicative of considerable concentration inhomogeneity.



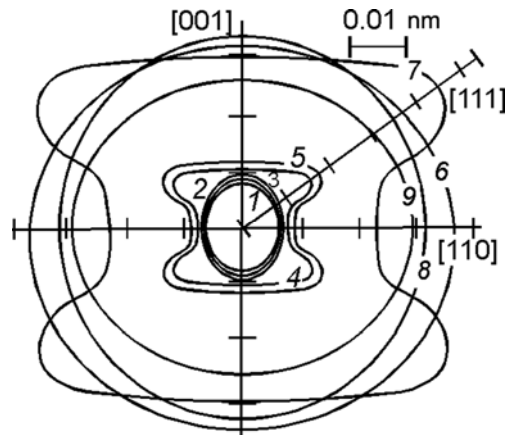


Fig. 7. Root-mean-square atomic displacements vs. different crystallographic directions in the (110) plane in the  $A1$ -phase at different temperature,  $T$ : 50 (curve 1), 150 (curve 2), 200 (curve 3), 240 (curve 4), 260 (curve 5), 650 (curve 6), 700 (curve 7), 750 (curve 8), and 800°C (curve 9).

We found out that in the two-phase region in the co-existing  $A1$  and  $B2$  phases, a certain periodic (this fact should be emphasized) re-distribution of concentrations of the alloy components is observed, which is made manifest in the formation of satellites near the main lines without affecting the lines themselves. The appearance of these satellites near the structural lines corresponds to the processes associated with low stability or instability of the crystal lattice with respect to the concentration waves [23]. A calculation within the framework of a simple model of one-dimensional sinusoidal modulations yields very different values of fluctuating concentration wavelengths (modulation period) in the  $B2$  ( $\lambda \sim (24 \pm 3)$  nm) and  $A1$  ( $\lambda \sim (7 \pm 3)$  nm) phases. The maximum value of atomic displacements due to this periodic redistribution of the alloy component concentration in the phases is equal to  $\sim 0.03$  nm, this being close to the total r.m.s. atomic displacements.

It should be noted that a common feature observed in the two-phase region is the presence of concentration inhomogeneities in the alloys under study in the course of the  $B2 \rightarrow A1$  and  $A1_{qu} \rightarrow B2 \rightarrow A1$  PTs, which possess their own peculiarities.

Thus, we have revealed a number of features in the structural-phase states of the Cu–Pd 40 at.% Pd alloys, which had not been reported in the available literature on equilibrium DOSs. It is important that the variations in the structural-phase state of the alloys of the Cu–Pd system near the concentration 40 at.% Pd are complicated by a few competing phenomena: atomic ordering, concentration inhomogeneity, and low-stability state or even crystal-lattice instability with respect to atomic displacements. This resulted in overlapping of two transitions in one and the same temperature interval: an order – disorder PT and a structural  $B2$ – $A1$  transition. The presence of the first-order  $B2$ – $A1$  transition exerts a certain influence on the temperature dependence of order parameter in the  $B2$ -phase, which, in turn, results in a stronger dependence of the shape of  $\eta(T)$  on the transition direction and alloy concentration. The  $B2$ – $A1$  PT invariably transits via the two-phase state of the alloy and is accompanied by concentration-induced splitting of the  $B2$  and  $A1$  phases in the DOS as well as concentration inhomogeneity. The character of this inhomogeneity depends on the initial phase state.

## 5. ANISOTROPY OF ATOMIC DISPLACEMENTS

Using the R. James's technique proposed in [30], from the experimental data of the temperature dependences of Bragg reflections we calculated the r.m.s. displacements of atoms from the average lattice sites in different crystallographic directions in the  $A1$ -structure phase (along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$ ), with the results presented in the projection on the (110) plane (Fig. 7). It is evident that as the temperature is increased in the region of low-stability

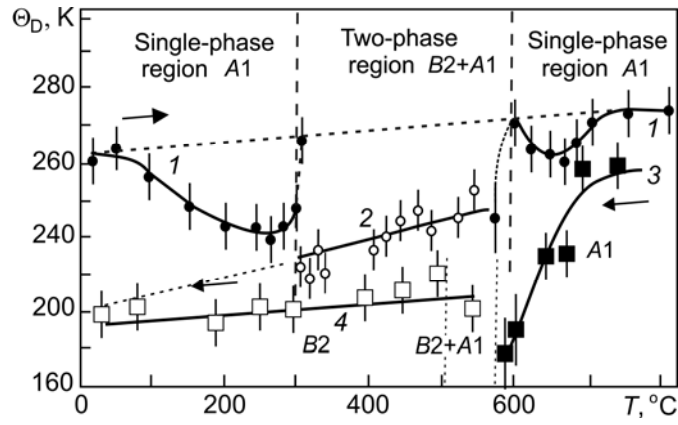


Fig. 8. Temperature dependences of the Debye temperature in the  $A1$  (curve 1) and  $B2$  (curve 2) phases under heating of the Cu – 36 at.% Pd alloy during the  $A1_{qu} \rightarrow (B2+A1) \rightarrow B2$  transitions and in the  $A1$  (curve 3) and  $B2$  (curve 4) under cooling of the Cu – 39.5 at.% Pd alloy during the  $A1 \rightarrow B2$  PT.

states preceding the irreversible (monotropic)  $A1_{qu} \rightarrow B2$  PT (similarly to the region following the reversible  $B2 \leftrightarrow A1$  PT), both the value and anisotropy of the total number r.m.s. displacements of atoms increase. At the temperatures 50°C higher than that of the end of the  $B2 \rightarrow A1$  PT, the r.m.s. atomic displacements are no longer anisotropic, and the number of completed r.m.s. displacements increases.

It is worth noting the results of atomic displacements in the (110) section of the fcc-lattice with respect to their size and that of the unit cell, which provide evidence of pronounced anisotropy of the completed atomic displacements in low-stability pre-transitional regions.

Both the anisotropy and the values of the averaged atomic displacements increase sharply as the temperature of the start of the  $A1_{qu} \rightarrow B2$  PT is approached; it should be noted that it is also in this temperature interval where the dependence of the lattice parameter on the disordered solid solution temperature deviates from the linear law. These phenomena indicate that prior to the PT the stability of crystal lattice of solid solution decreases (low-stability state develops) with respect to the displacement of atoms from the crystal lattice sites.

From the temperature dependences of the Debye – Waller factor calculated from the main interference lines of the ordered  $B2$  phase (without distributing the displacements of atoms of different kinds over sublattices of the  $B2$  phase) and the disordered  $A1$  phase during the  $A1_{qu} \rightarrow B2$  PT we calculated the temperature dependences of the Debye temperature  $\Theta_D$  (Fig. 8). The temperature  $\Theta_D$  (calculated to anisotropic approximation in the disordered  $A1$  phase) prior to the  $A1_{qu} \rightarrow (B2+A1)$  transition exhibits a nonlinear behavior (Fig. 8, curve 1). The decrease in  $\Theta_D$  (to the values close to the Debye temperature in the  $B2$  phase) observed in the  $A1$  phase before the transition indicates a decrease in stability of the crystal lattice (a low-stability state is developed). Thus the analysis of the dependence of the Debye temperature calculated in the isotropic approximation shows that there are low-stability pre-transitional states in the disordered phase.

## 6. ATOMIC DISPLACEMENTS IN THE ORDERED $B2$ PHASE IN THE TWO-PHASE REGION

The r.m.s. displacements in the ordered  $B2$ -structure phase formed by heating up to the temperatures higher than 300°C following the  $A1_{qu} \rightarrow B2$  PTs were measured in different sublattices occupied by the palladium and copper atoms (Fig. 9). The value of the r.m.s. displacements of copper atoms is larger than that of palladium atoms, and the ratio  $\langle u_{tot}^2 \rangle_{Cu} / \langle u_{tot}^2 \rangle_{Pd} = 1.9$  is inversely proportional to the ratio of their masses  $(m_{Cu} / m_{Pd})^{-1} = 1.7$ .

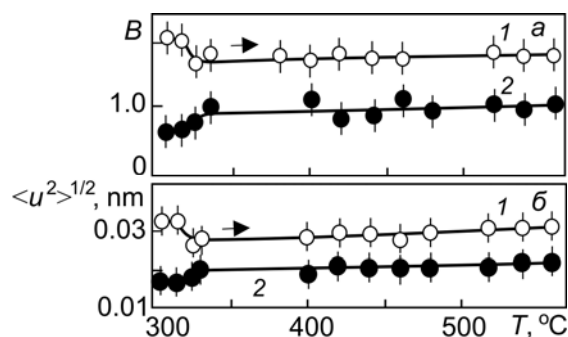


Fig. 9. Temperature dependences of the Debye temperature as a function of the Debye – Waller factor  $B$  (a) and the total r.m.s. displacements of atoms (b) in the  $B2$  phase following the  $A1_{qu} \rightarrow (B2+A1)$  PT in the Cu – 36 at.% Pd alloy (curves 1 and 2 were calculated from the main line intensities and those of the superstructure lines, respectively (a), curves 1 and 2 are the Cu and Pd atom displacements in the  $B2$  superstructure sublattices, respectively (b).

The r.m.s. atomic displacements increase linearly with the temperature within 300–500°C. The singularity is observed in the narrow region only immediately after the  $A1_{qu} \rightarrow B2$  transition, where with increased temperature there is a non-monotonous variation in the r.m.s. atomic displacements in the  $B2$  superstructure sublattices.

## 7. MANIFESTATION OF THE EFFECTS OF ANHARMONICITY OF ATOMIC VIBRATIONS IN THE CRYSTAL LATTICE DURING PHASE TRANSITIONS IN CuPd ALLOYS

The results of experimental investigations on determination of the temperature dependences of the integral characteristics (Debye–Waller factor, atomic displacements, and characteristic temperature) can be used to analyze interatomic interactions in crystals. It is well known [31] that non-linearity of the temperature dependences of the integral dynamic characteristics is due to anharmonicity of the integral interatomic interactions. An analysis of the dynamic parameters and variation in the structural states of the CuPd alloys allowed us identify a certain correlation. The change of the structural state of the phase is accompanied by the changes of its dynamic properties.

In the CuPd alloys, where the main structural transition is a  $bcc \leftrightarrow fcc$  transition, the r.m.s. atomic displacements in the temperature interval in the region of low-stability states preceding the PT are anisotropic. ‘Softening’ of the lattice in the fcc-phase is observed along the  $\langle 111 \rangle$  direction, i.e., the atoms in the fcc-lattice structure start preparing for rearrangement into a bcc-coordination.

Thus, in the high-temperature region in the vicinity of the structural PT preliminary phenomena and low-stability states. A few degrees before the temperature of the start of a structural PT, intraphase transformations take place, which prepare the phase to a real transition [31].

## SUMMARY

In this work low-stability state and peculiarities of structural changes in the region of phase transitions have been presented using the Cu–Pd alloys containing ~40 at.% Pd as an example. To this aim we have determined *in situ* the crystal lattice parameters, the long-rang atomic order parameters, and the Debye – Waller factor in the  $B2$  and  $A1$  phases, using X-ray diffraction examination immediately in the temperature intervals of the structural  $B2 \rightarrow A1$  transition and the order – disorder phase transition. Based on the X-ray diffraction data, an analysis has been made of the peculiarities of the  $B2$  and  $A1$  phases in the CuPd alloys in the vicinity of structural phase transitions and the behavior pattern of atomic vibrations in the crystal lattice. It has been shown that close to the structural-phase transformations in the CuPd alloys containing ~40 at.% Pd low-stability states are realized, which represent a number of anomalous

phenomena (such as anisotropy of atomic displacements, concentration inhomogeneity, splitting, heterophase fluctuations, non-linearity in the lattice parameter and long-range order parameter dependences, etc.) preparing the system for transformation.

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