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Crystallographic Parameters of Compounds and Solid Solutions in Binary Systems Cu-Pt and Ga-Pt

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Abstract. The study establishes that the packing index in compounds of the system Cu-Pt is close to the value 0.74 against a slight deviation from the Zen law of atomic volumes. The compounds in the system Ga-Pt have the highest values of the packing index in the range of the equiatomic composition, which greatly exceed ψ for close-packed structures based on FCC and HCP lattices for compounds made of the same kind of atoms. A correlation between singular points on the phase diagram of the system Ga-Pt and high values of the packing index in compounds is established.

INTRODUCTION

The systems Cu-Pt and Ga-Pt are unique. This is primarily associated with a number of interesting peculiarities of these systems. First of all, the system Cu-Pt is the only system, in which alloys during the phase transition (PT) order-disorder from a disordered state of a regular solution based on the FCC lattice (structure A1) transition into a number of crystallographic structures [1, 2]. Secondly, in alloys of the system Cu-Pt there are states with a variety of superstructures ($L1_2$, $L1_1$, $L1_3$, $L1_0$) in a wide concentration range of components of the binary alloy, and are formed from the structure A1 into geometrically close-packed structures [1–3]. Thirdly, a weak stability or instability of the crystalline lattice is observed in temperature ranges preceding PT [4].

Another situation is observed in the system Ga-Pt, in which the whole spectrum of ordered compounds (Ga_6Pt, Ga_7Pt_3, Ga_2Pt, Ga_3Pt_2, GaPt, Ga_3Pt_5, β-$GaPt_2$, α-$GaPt_2$, γ′-$GaPt_3$) is formed either directly from a liquid phase, or as a result of peritectoid reactions [1, 5–7]. At the same time, some Ga-Pt-based compounds are topologically close-packed.

It is believed that combining the phase transition order-disorder with structural-phase transitions in the system Cu-Pt and a wide temperature range of compound formation in the system Ga-Pt (from 290 up to 1370°C), creates new opportunities for controlling the structure and mechanical properties of metallic alloys.

The paper presents the results of a search for a correlation between crystal-geometry parameters and peculiarities of structure-phase states in alloys with well pronounced pretransitional states in the system Cu-Pt and weakly pronounced pretransitional states in the system Ga-Pt using the concept that crystalline structures can be represented as multi-level multistage systems.

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DEVIATION FROM ZEN LAW AND THE PACKING INDEX IN ALLOYS OF BINARY SYSTEMS Cu-Pt AND Ga-Pt

During crystallization, alloys of the system Cu-Pt form a continuous series of solid solutions based on the FCC lattice with a structure A1. Ordered structures with stoichiometric compositions Cu_3Pt, CuPt, $CuPt_3$, and $CuPt_7$ begin to form in this system from temperatures of 800°C in a wide range of concentrations [1].

Complex elementary cells of intermetallic compounds are described as multi-level multistage systems [8, 9]. For example, a distinctive feature of the binary system Cu-Pt is the fact that a rhombohedral superstructure $L1_1$ ($D_{3d}^5 - R\bar{3}m$) with 54 atoms per elementary cell forms in this system in the region of the equiatomic composition. All Hume-Rothery conditions for the formation of wide ranges of continuous solid solutions are carried out for the system Cu-Pt [10]. On the other hand, in the system Ga-Pt the ranges of solid solutions are limited, and mainly intermetallic compounds with 12−16 atoms per unit cell are formed.

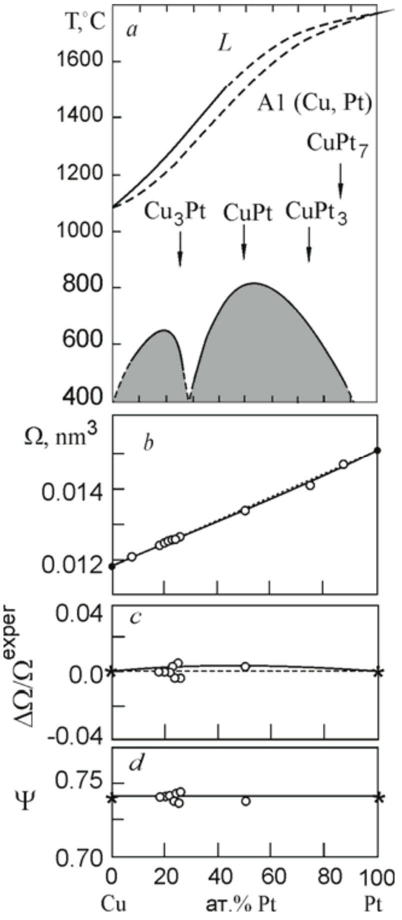

FIGURE 1. Phase diagrams (a) [1, 2] and dependences of atomic volumes (b) [16], the relative magnitude of the superstructure compression (c), and the packing index (d) on the concentration in compounds of the system Cu-Pt

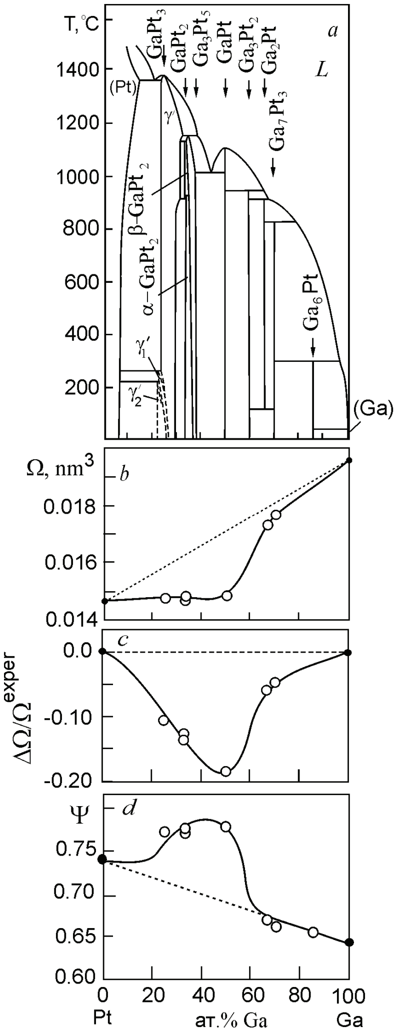

FIGURE 2. Phase diagrams (a) [1, 5–7] and dependences of atomic volumes [16] (b), the relative magnitude of the superstructure compression (c), and the packing index (d) on the concentration in compounds of the system Ga-Pt

To find general laws of stability of structural compounds in the investigated binary systems the following set of crystallogeometrical parameters was used [11–13]: the atomic volume of elements Ω; the value of deviation from the linear dependence of the atomic volume $\Delta\Omega/\Omega^{\text{exp}} = (\Omega^{\text{exp}} - \Omega_3)/\Omega^{\text{exp}}$ on the concentration (Ω^{exp} is the atomic volume in the alloy determined from the experimental values of parameters of elementary cells of the alloy, Ω_3 is the atomic volume determined by Zen law [14, 15]); and the space filling index ψ proposed by Laves-Parte [15], which characterizes the density of space filling by different types of atoms with different crystalline structures.

In the system Cu-Pt it has been established that in the solid solution with a disordered structure A1 and in ordered compounds with $L1_2$ and $L1_1$ structures the values of the packing index ψ are close to the value 0.74, and this is accompanied by a very weak positive deviation on concentration dependences of the atomic volume from Zen law (Fig. 1). The phase diagram of the system Ga-Pt contains singular points conditioned upon formation of a wide range of compounds [1, 5–7]: Ga_6Pt, Ga_7Pt_3, Ga_2Pt, Ga_3Pt_2, GaPt, Ga_3Pt_5, β–$GaPt_2$, α–$GaPt_2$, $GaPt_3$ (Fig. 2). A number of peculiarities should be noted. First of all, Ga has an electronic structure significantly different from the structure of elements Cu and Pt. Secondly, the melting temperature of Ga is anomalously low, as compared to conventional metals. Unlike the system Cu-Pt, which has no singular points on the concentration dependence of the melting temperature, in the system Ga-Pt the greatest deviation in the concentration dependence of the atomic volume from Zen law is observed in the range of the equiatomic composition, which correlates with high melting temperatures that correspond to formation of intermetallic compounds (Fig. 2).

The calculated concentration dependences of the packaging index ψ (based on experimental values of crystalline lattice parameters [1, 5–7]) in compounds in the region of the equiatomic composition GaPt (structure B20, prototype FeSi) and Ga_3Pt_2 (structure $D5_{19}$, prototype Al_3Ni_2) are shown in Fig. 2. It can be seen that in the system Ga-Pt the compounds have the highest values of the packing index in the region of the equiatomic composition, which are considerably superior to ψ for close-packed structures based on FCC and HCP lattices for compounds made of the same kind of atoms.

It is believed that such a correlation between singular points on the phase diagram of the system Ga-Pt and high values ψ reflects an increase in interatomic interaction forces and the growth in covalent and ionic components of the interaction between atoms with respect to the metal one. Meanwhile, a different situation occurs in the system Cu-Pt which has no singular points on the concentration dependence from the melting temperature, and this is accompanied by a slight deviation from Zen law. Lowering the temperature in the range of 600–800°C leads to phase transitions into ordered phases Cu_3Pt, CuPt, $CuPt_3$ and $CuPt_7$.

THE HIERARCHY OF STRUCTURAL ELEMENTS IN CRYSTALLINE STRUCTURES

Often in the literature analysis of various crystalline structures is carried out by allocating similar structural fragments, which then form complex crystalline systems. This allows a generalization of transformation methods, with the use of which one or another structural type is obtained [8, 9]. The basic principles of this classification are based on the fact that similar positions of a part of atoms are retained in structural types, which are derived from the initial ones by replacing a part of atoms with pairs, groups of atoms, or an alternation of layers with a different configuration of atoms. Structural types obtained from the initial ones by a multiple replacement can be characterized by a different distribution of a part of replacing atoms and groups of atoms [8, 9].

Structural types, built of identical fragments and located differently with respect to each other, are called homotypic [8]. A special case of homotypic structures are ordered structures Cu_3Pt, CuPt, $CuPt_3$ and $CuPt_7$ in the system Cu-Pt [17]. It is important to note that structural types may have similar positions of atoms, but can differ in the number of components substituting these positions. The symmetry and the shape of elementary cells may change simultaneously [8, 9]. The orderly replacement of leveling point systems with various atoms leads to formation of superstructures. Superstructures can be formed at a permanent number of components as a result of their redistribution along leveling point systems. Division of a set of structural types of intermetallic compounds into classes is carried out by types of coordination polyhedrons peculiar to atoms. This approach was used to analyze crystalline structures in systems Cu-Pt and Ga-Pt.

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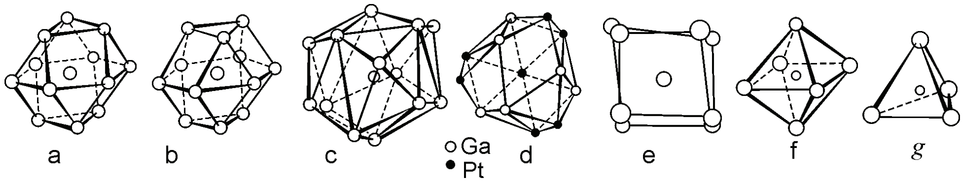

FIGURE 3. Coordination figures ща atoms in structures of compounds with different classes: (a) class 1 cuboctahedron and its hexagonal analogue; (b) with a coordination number CN = 12; (c) Class 4 a 13-vertex polyhedron in the structure B20 with CN = 7 + 6 for the compound GaPt; (d) a 7-vertex octahedron $PtGa_7$ and a tetrahedron in the structure PtGa; (e) class 8 defective rhombic dodecahedron (cube plus a defective octahedron, CN = 8 + (6 − *m*'); (f) Class 11 octahedron (CN = 6); (g) class 14 tetrahedron (SC = 4)

The orderly replacement of leveling point systems with various atoms leads to formation of superstructures. Superstructures can be formed at a permanent number of components as a result of their redistribution along leveling point systems. Division of a set of structural types of intermetallic compounds into classes is carried out by types of coordination polyhedrons peculiar to atoms. This approach was used to analyze crystalline structures in systems Cu-Pt and Ga-Pt. In the system Cu-Pt all compounds belong to the 1st class of crystalline structures according to classification [9]. The structures of this class have a total coordination number CN = 12, and can be presented as a coordination polyhedron in the shape of an octahedron and (or) its hexagonal analogue (Figs. 3a and 3b). In the case when atoms in a compound can be represented as closest packs of spheres of equal size, the packing index $\psi = \pi 3/\sqrt{2}\times 100\% = 74.05\%$. Superstructures can be obtained from these polyhedrons as their corresponding deformed derivatives. From tetragonal deformed derivatives of cubic closest packing the structures with the ratio of periods (in a face-centered aspect) greater than $\sqrt{2}/2$ belong to this class.

It is important that in this classification [9] the structural class types are classified according to the type of closest packing or by the composition or the stoichiometric type. As shown in [17], eight spatial groups are possible for closest packings. In the system Cu-Pt the compounds Cu_3Pt(*Pm-3m*), CuPt (*R*3*m*) $CuPt_3$(*Fm*-3*m*) belong to this group of closest packings.In structures with the composition LM_3 a derivative from one closest packing with layers of the same composition, the atom L is surrounded similarly in the first coordination sphere. The structure of the alloy affects the distribution of atoms L and M in the more remote coordination spheres. In the structure $L1_2$ (Cu_3Pt) at a distance from the central atom ($\sqrt{2}$ times greater than the minimum distance) there are 6 atoms of the kind L, and at a distance greater than $\sqrt{3}$ times—24M.

In the system Ga-Pt there is another situation. In this system the compounds belong to different classes of crystalline structures [9]: Ga_2Pt (8, 14, *Fm*-3*m*), Ga_3Pt_2 (8, *P*3*m*l), GaPt (4, $P2_13$), Ga_3Pt_5 (1, *Cmmm*), $\beta GaPt_2$ (14, *Pbam*), $GaPt_3$(1, *Pm*3*m*). The number of classes of crystalline structures according to the classification [9] and their spatial groups are shown in parentheses. The compound Pt_3Ga with the composition LM_3 belongs to the 1st class of crystalline compounds, as well as all compounds in the system Cu-Pt. The compound Pt_3Ga with the composition LM_3 and the compound Pt_5Ga_3 with the composition L_3M_5 belong to the 1st class of crystalline structures (Fig. 4) with a rhombic cubic closest packing. The closest layers of the compound Pt_5Ga_3 can be formed from fragments of simpler structures—$L1_2$ and $L1_0$ (Fig. 4). In structures L_3M_5 the ratio $LM_3 : LM$ in the layer equals to 1 : 2. The compound GaPt (FeSi prototype) with the composition LM belongs to the 4th class of crystalline structures (Fig. 3) [9].

A coordination polyhedron of this class belongs to a 13-vertex of the type FeSi with CN = 13 (Fig. 3c). According to [17], the structure of FeSi is formed during a strong internal deformation of the structure of the 11th class (Fig. 3e), which contains the same number of atoms in a cubic elementary cell as FeSi (class 8, Fig. 3d).

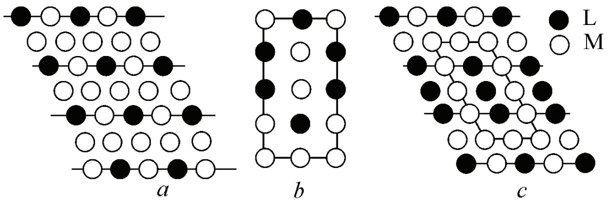

FIGURE 4. The layer LM_3 in the compound Pt_3Ga with the structure $L1_2$ (a), in the compound AuCu-I with the structure of $L1_0$ (b), and in the compound with the structure Pt_3Ga_5 B20 (c)

The structure GaPt can be represented as a stacking of 7-vertexes [$FeSi_7$] (4 per elementary cell) and an equal number of empty trigonally deformed tetrahedrons, each 7th-vertex is adjacent to edges of 6 similar polyhedrons and four tetrahedrons; 7-vertexes alternate with tetrahedrons along triad axes.

The compound $PtGa_2$ with the composition $L2_M$ belongs to the 8th class of crystalline structures [9] (Fig. 4). The structures of this class are coordination polyhedrons: a defective rhombic dodecahedron (CN = $(8 - m') + 6$ or $8 + (6 - m'')$) has a number of derivatives resulting by subtracting atoms. In addition to derivatives from structures A1 and B2, structures with defective rhombic-dodecahedron coordination belong to the 8th class. The compound $\beta GaPt_2$ with the composition LM_2 belongs to the 14th class (Fig. 3). The prototype of this compound is the structure Ge_3Rh_5, which is based on the stacking of two (per cell) corrugated layers [9]. Thus, the presence of close-packed layers and the appropriate mix of distorted coordination polyhedrons in compounds of the system Ga-Pt lead to a noticeable increase in values of the packing index in these compounds. While in the system Cu-Pt, there is an alternation of close-packed layers within the 1st class, and the packing index is close to 0.74.

CONCLUSION

The conducted analysis of crystallographic parameters of compounds and solid solutions in the binary systems Cu-Pt and Ga-Pt allows us to make a conclusion that a wide range of structural-phase states and corresponding values of crystallographic parameters indicates their weak stability against interconversions under small changes in external conditions. The structure-phase states are thermodynamically similar, but crystallographically they differ significantly.

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