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Vasyl Stefanyk Precarpathian
National University

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M. Raransky, A. Oliinych-Lysiuk., R. Tashchuk, A. Tashchuk, A. Struk, M. Unguryan

Auxetic properties of some intermetallic compounds

Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine, m.raransky@chnu.edu.ua

With the application of a linear theory of elasticity of anisotropic crystals and the use of experimental values of elastic moduli C_{ij} and compliances S_{ij} given in the Landolt-Börstein tables, characteristic surfaces of Young's moduli, angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ and indicating auxeticity surfaces of single crystals of intermetallic compounds *Ag-Au, Cu-Ni, Cu-Au,* and *Cu-Zn* were for the first time constructed.

The extremely high sensitivity of the component of the extreme values of Young's moduli $E_{<110>}$ to anomalous deformations during phase transformations of the order-disorder type was established. Anomalies of the concentration dependences of the auxetic parameters $\mu_{min}(X)$, $\mu_{max}(X)$ and the auxeticity degree $S_a(X)$ near the points of phase transformation of the second order type were revealed.

Keywords: auxetic, Young's moduls, Poisson's ratios, anomalous deformations, anisotropy, elastic properties.

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Introduction

Intermediate phases in state diagrams that have a predominantly metallic type of chemical bond are called intermetallic compounds. The variety of properties of intermetallic compounds ensures their wide practical application. The crystal structure of these phases, as a rule, differs from the structure of the components that form it. Solubility limits of components in the solid state and the conditions for the formation of stable intermediate phases are determined by the semi-empirical Hume-Rothery rules. If the crystal lattices of components *A* and *B* are isomorphic, and the difference in atomic radii $\Delta r=(r_A-r_B)$ does not exceed 8-15%, then substitutional solid solutions with unlimited solubility of the components are formed [1]. During heat treatment of solid solutions, processes of redistribution of atoms can occur, as a result of which the atoms of the components will occupy certain defined positions in the nodes of the crystal lattice, forming superstructures. Such processes are called ordering and are accompanied by a change in physical and mechanical properties [2]. Ordered solid solutions can be considered as intermediate phases between solid solutions and chemical compounds.

Of all the intermediate phases with a wide range of component solubility, the metallic nature of the chemical bond is most pronounced in electronic compounds (Hume-Rothery phases) [3]. The crystal lattices of these compounds also differ from the lattices of the components that make them up, and their stability is determined by the electronic configuration, that is, the ratio of the number of valence electrons to the number of atoms in the compound $n=c/a$. Electronic compounds are homogeneous in a wide range of concentrations.

The physico-chemical and mechanical properties of the above-mentioned intermetallic compounds, as a result of their wide application, have been thoroughly studied [1-3]. At the same time, the auxetic properties of these compounds are not well known. We are aware of only a few scientific works [4-7] in which Young's moduli E, shear moduli G_s and Poisson's ratios μ are determined for some single crystals of cubic system in certain crystallographic directions. However, to analyze the anisotropy of elastic properties of single crystals, it is necessary to construct the characteristic surface of Young's moduli. The angular distribution of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ can be constructed only with fixed values of one of the Euler angles φ, Θ, ψ, that is, it is impossible to construct a four-dimensional surface in a three-dimensional coordinate system. Therefore, identifying the mechanisms and regularities of the formation of auxetic surfaces in crystals is a rather difficult task.

In this work, using the theory of elasticity of anisotropic solids, modern methods of physical acoustics and computer technology for processing experimental results, programs were created that allow one to construct the characteristic surfaces of Young's moduli E_i, angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ and indicating auxetic surfaces for single crystals of arbitrary systems.

The analysis of the auxetic properties of *Ag-Au, Cu-Ni, Cu-Au, Cu-Zn, Cu-Al* intermetallic alloys was carried out using the experimental values of the elastic moduli C_{ij} and compliances S_{ij} given in [8]. The characteristic surfaces of Young's moduli were constructed and the extreme values E_{min} and E_{max} of the studied single crystals were determined. It was established that the negative values of Poisson's ratios $\mu_{min}<0$ are concentrated around some crystallographic directions and form indicating auxetic surfaces in space. The basic conditions and regularities of the formation of axial and non-axial auxeticity of cubic system single crystals have been revealed. The transformations of auxeticity indicating surfaces that occur during phase transitions in the processes of ordering in solid solutions and the appearance of superstructures and the formation of complex electronic compounds (Hume-Rothery phases) in intermetallic compounds were studied.

This study is a continuation of the cycle of works on the study of the anisotropy of elastic properties, the formation of auxetic properties and the dynamics of crystal lattices of single crystals of various systems.

I. Theoretical foundations

The vast majority of the intermetallic compounds studied by us have a cubic lattice. The presence of axes of the 3d and 4th orders in the cubic system causes the appearance of the following relationships between the components of the elastic moduli (in the Voigt notation) [9]

$$C_{11} = C_{22} = C_{33};\ C_{44} = C_{55} = C_{66};$$

$$C_{12} = C_{13} = C_{23};\ C_{45} = C_{46} = C_{56} = 0 \qquad (1)$$

and the matrix of elastic moduli will be written in the form:

$$C_{ij} = \begin{vmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{vmatrix} \qquad (2)$$

As follows from (2), there are only three independent components of the elastic modulus C_{11}, C_{12}, C_{44} for cubic system crystals. Note that the matrix C_{ij}, as well as S_{ij} are not second-rank tensors and their components are not transformed as tensor components. The relationship between the elastic moduli C_{ij} and compliances S_{ij}, for a given system, is as follows

$$C_{11} = \frac{S_{11}+S_{12}}{(S_{11}-S_{12})(S_{11}+2S_{12})};\quad S_{11} = \frac{C_{11}+C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})};$$

$$C_{12} = \frac{-S_{12}}{(S_{11}-S_{12})(S_{11}+2S_{12})};\quad S_{12} = \frac{-C_{12}}{(C_{11}+C_{12})(C_{11}+2C_{12})}; \qquad (3)$$

$$C_{44} = \frac{1}{S_{44}};\quad S_{44} = \frac{1}{C_{44}}$$

For isotropic crystals, the components C_{ij} and S_{ij} at certain ratios acquire a certain physical meaning, which can be compared with known technical characteristics of materials, such as Young's modulus E, shear modulus G_s, and Poisson's ratio μ:

$$E = \frac{1}{S_{11}};\quad G_S = \frac{1}{2}(C_{11} - C_{12});$$

$$G_S = \frac{1}{2}(C_{11} - C_{12});\ \mu = \frac{S_{12}}{S_{11}} \qquad (4)$$

For anisotropic solids of cubic symmetry, Young's modulus is equal to [9]:

$$(E_n)^{-1} = S_{11} - (2S_{11} - 2S_{12} - S_{44})(n_1^2n_2^2 + n_1^2n_3^2 + n_2^2n_3^2) \qquad (5)$$

where n_1, n_2, n_3 are direction cosines.

From the relation (5) it follows that when one of the factors is equal to zero, $(E_n)^{-1} = S_{11}$, like for the isotropic crystals. The second factor $(n_1^2n_2^2 + n_1^2n_3^2 + n_2^2n_3^2) = 0$ only in crystallographic directions *<100>*. If the second factor $(2S_{11} - 2S_{12} - S_{44}) = 0$, then $E_n=1/S_{11}$ in all directions, that is, the crystal will be elastically isotropic. From the condition of isotropicity of cubic system crystals $(2S_{11} - 2S_{12} - S_{44}) = 0$ it follows [10]:

$$A = \frac{2(S_{11}-S_{12})}{S_{44}} = \frac{2C_{44}}{C_{11}-C_{12}} = 1 \text{ or } A = \frac{2C_{44}}{G_S} = 1 \qquad (6)$$

where G_s is shear modulus which for *Cu, Ag, Au, CuAu, CuAl, CuZn* crystals is equal to [9]:

$$G_S^{-1} = \frac{4}{3}(S_{11} - S_{12}) + \frac{1}{3}S_{44} \qquad (7)$$

From the relations (5) – (7) it is easy to obtain the expression for the extreme values of Young's modulus

$$E_{(100)} = \frac{1}{S_{11}};\quad E_{(110)} = \frac{1}{S_{11} - \frac{1}{4}S_{44}(A-1)};$$

$$E_{(111)} = \frac{1}{S_{11} - \frac{1}{3}S_{44}(A-1)} \qquad (8)$$

For single crystals of cubic system the Poisson's ratio is given by [10]:

$$\mu'_{ij} = -\frac{\left[\begin{array}{c}(\alpha_{11}^2\alpha_{21}^2+\alpha_{12}^2\alpha_{22}^2+\alpha_{13}^2\alpha_{23}^2)S_{11}+(\alpha_{11}^2\alpha_{22}^2+\alpha_{12}^2\alpha_{21}^2+\alpha_{11}^2\alpha_{23}^2+\alpha_{13}^2\alpha_{21}^2+\alpha_{12}^2\alpha_{23}^2+\alpha_{22}^2\alpha_{13}^2)S_{12}+\\ +(\alpha_{12}\alpha_{13}\alpha_{22}\alpha_{23}+\alpha_{11}\alpha_{13}\alpha_{21}\alpha_{23}+\alpha_{11}\alpha_{12}\alpha_{21}\alpha_{22})S_{44}\end{array}\right]}{[(\alpha_{21}^4+\alpha_{22}^4+\alpha_{23}^4)S_{11}+(2\alpha_{21}^2\alpha_{22}^2+2\alpha_{21}^2\alpha_{23}^2+2\alpha_{22}^2\alpha_{23}^2)S_{12}+(\alpha_{22}^2\alpha_{23}^2+\alpha_{21}^2\alpha_{23}^2+\alpha_{21}^2\alpha_{22}^2)S_{44}]} \quad (9)$$

where $\alpha_{f(ijkl)g(mnop)}$ are direction cosines, and $f, \mathrm{g} = 1, 2,3$.

The relations (5), (7), (9) were used to construct the characteristic surfaces of Young's moduli and the indicating auxeticity surfaces of single crystals under study.

II. Discussion of results

a) Unlimited solid solutions.

The study of the mechanisms and regularities of the formation of indicating auxeticity surfaces should be started with the alloys, the components of which have full continuous mutual solubility in both the liquid and solid states. These requirements are met by *Ag-Au* alloy. The difference in atomic radii is *0* ($r_{Ag}=r_{Au}=0.144$ *nm*). The crystal lattice constant of the alloy continuously increases from $a_{Au}=0.4078$ nm to $a_{Ag}=0.408624$ nm. The absence of superstructural lines on *X*-wave diffractograms, that is, the absence of ordering processes in *Ag-Au* alloys, was proven by specially conducted studies. [1].

Fig.1 shows the characteristic surfaces of Young's moduli, angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$, and indicating auxeticity surfaces of *Ag-Au* alloys. The characteristic surfaces of Young's moduli have a similar shape, just as for pure metals Cu, Ag, Au [10]. The anisotropy of the crystals, calculated from relation (6), increase from $A_{Au}=2.88$ to $A_{Ag}=9.01$, as does the length of the chemical bond ($a_{Au}=0.4078$ *nm* to $a_{Ag}=0.408624$ *nm*). The experimental values of Young's moduli, calculated according to relation (8), reach maximum values at 50% *Au* and, accordingly, are equal to [5]: $E_{[100]}=50.8$*GPa;* $E_{[110]}=$ *95.1 GPa;* $E_{[111]}=$ *134.0 GPa.* The maximum hardness value is achieved by *Ag-Au* alloys containing 50% Ag: $H_B = 28$ *кg/mm²* [1].

The regularities of formation of the characteristic surfaces of Young's moduli of cubic system single crystals are described in [10].

Due to the presence of 2nd, 3rd, and 4th order axes in cubic system crystals, the function $\mu(\varphi, \Theta, \psi)$ is periodic with period π, and the surface of the angular distribution $\mu(\varphi, \Theta, \psi)$ is formed both by positive $\mu > 0$, as well as negative $\mu < 0$ values. Recall that $\mu(\varphi, \Theta, \psi)$ can be constructed only at fixed values of one of the Euler angles φ, Θ or ψ (in Fig. 1, b $\varphi = 0$).

An insignificant part of the negative values of $\mu_{min}<0$ is concentrated in symmetrically equivalent crystallographic directions <110>, forming indicating auxeticity surfaces of single crystals of the *Ag-Au* alloy (Fig. 1, c). As *Au* % increases, the negative values of Poisson's ratio μ_{min} grow, gradually approaching zero (Fig. 2)

Note that for *Ag-Au* alloys, as well as for the vast majority of cubic system crystals, negative μ_{ij} values are observed in crystallographic directions <110> - non-axial auxeticity. A necessary and sufficient condition for the occurrence of non-axial auxeticity for cubic system crystals is [10]:

$$S_{11} + S_{12} - \tfrac{1}{2}S_{44} > 0 \quad (10)$$

The area of indicating surfaces S_a (or the auxeticity degree) gradually decreases in proportion to the decrease in the elastic anisotropy factor *A* and concentration *X* (Fig. 3). Therefore, for continuous *Ag-Au* substitutional solid solutions, with increasing *X* concentration, all auxetic properties (μ_{min}, μ_{max} S_a) change linearly, as expected.

In the *Cu-Ni* alloy, both components have a *fcc* lattice, the periods of which are $a_{Cu}=0.361479$ *nm;* $a_{Ni} = 0.352430$ *nm* ($\Delta a = 0,009043$ *nm*). *The fcc* lattice is preserved in the entire range of temperatures and concentrations. The atomic radii are equal: $r_{Cu}=0.128$ *nm,* $r_{Ni}= 0.124$ *nm* [1]. The average deviation of the values of the atomic radii is not exceed 3%, which fully meets the requirements of the Hume-Rothery rule, necessary for the formation of a continuous series of substitutional solid solutions. Therefore, the *Cu-Ni* alloy can serve as an ideal example of unlimited solubility of components in the solid state.

For single-crystal *Cu-Ni* samples, when *Cu* atoms are completely replaced by *Ni*, a change in the main values of mechanical parameters should be expected within the limits of:

$E_{<111>}(Cu)= 190{,}0$ *GPa* → $E_{<111>}(Ni)=300$ *GPa*

$G_s(Cu)=23.4$ *GPa* → $G_s(Ni)=45.4$ *GPa*

$\mu_{min}(Cu)= - 0.13$ → $\mu_{min}(Ni)= - 0.01$

$\mu_{max}(Cu)= + 0.8$ → $\mu_{max}(Ni)= + 0.65$

In [5], for *Cu* and *Ni* single crystals the following values of Poisson's ratios were obtained: $\mu_{min}(Cu)=-0.13$; $\mu_{max}(Cu)=+0.8$; $\mu_{min}(Ni)=-0{,}07$; and the average values for polycrystals are known to be equal to $<\mu>(Cu)= + (0.31 – 0.34)$; $<\mu>(Ni)=+ (0.27 – 0.31)$. Thus, during the formation of a substitutional solid solution the replacement of atoms of solvent (*Cu*) by the atoms of dissolving element (*Ni*), which are distinguished by somewhat smaller size of atoms (*2.75%*), should lead to a gradual linear compression of the alloy crystal lattice. In conformity with Vegard's law, in this case, a linear dependence of crystal lattice periods on the concentration *a(X)* should be observed. Similar concentration dependence can be found for other physical and mechanical parameters of solid solutions (see Fig. 2, Fig. 3 for *Ag-Au* alloys).

Fig. 5 shows the concentration dependences of Poisson's ratios μ_{min} and μ_{max} and Fig.6 – the concentration dependences of the auxeticity degree S_a for *Cu-Ni* alloys. Despite the smooth change in concentration at *X= 70%*, there is a sharply expressed anomaly of the $\mu_{min}(X)$, $\mu_{max}(X)$ та $S_a(X)$ dependences, which is not typical for continuous substitutional solid solutions.

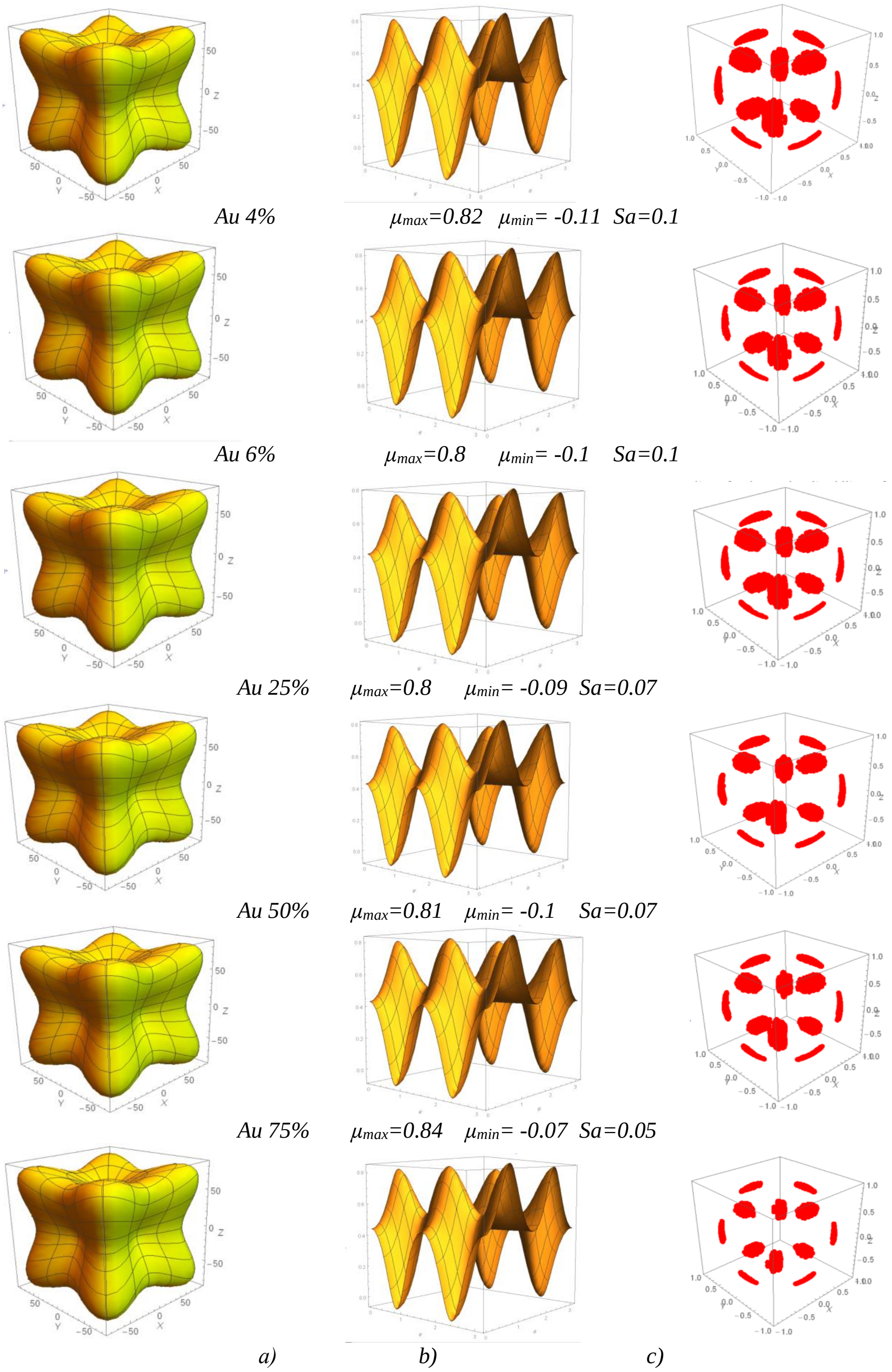


Fig.1. Characteristic surfaces of Young's modulus *(a)*, angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$ *(b)* and indicating auxeticity surfaces of single crystals *(c)* of *Ag-Au* alloys.

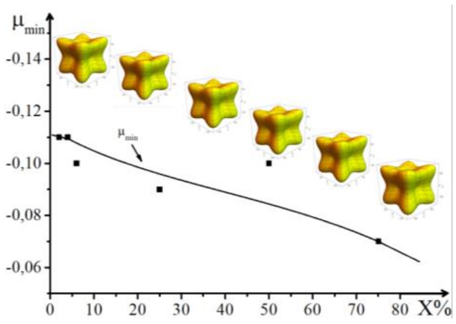


Fig.2. Dependence of Poisson's ratio μ_{min} for *Ag-Au* alloy on the concentration *X* of *Au*.

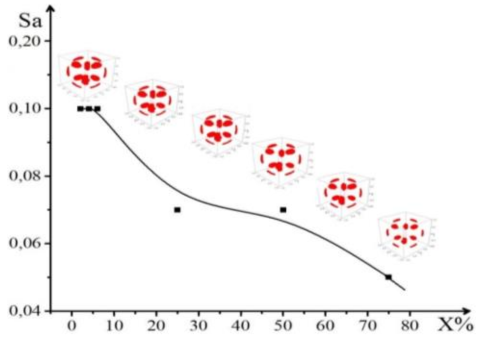
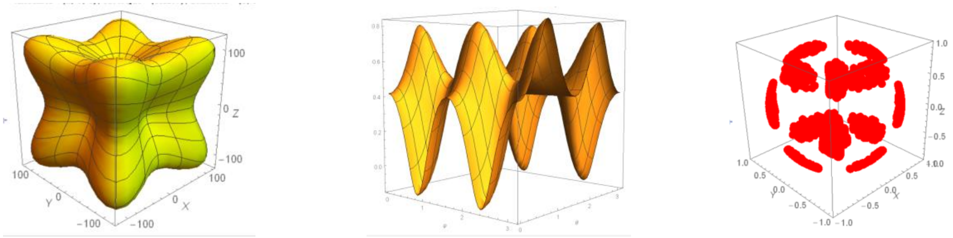
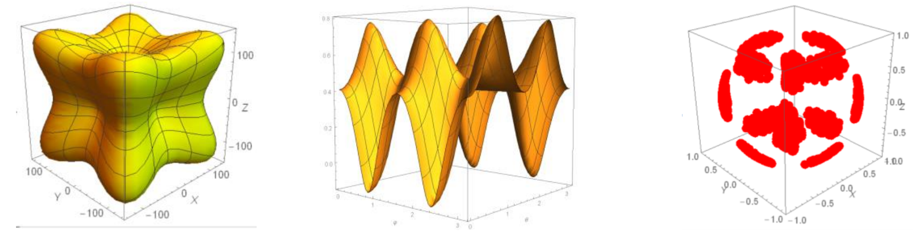


Fig.3. Dependence of auxeticity degree S_a on the concentration *X* for *Ag-Au* alloy.

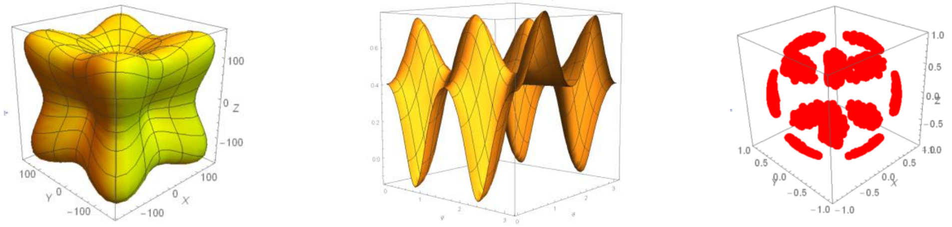
Ni 2.34% $\mu_{max}=0.8$ $\mu_{min}= -0.17 Sa=0.15$



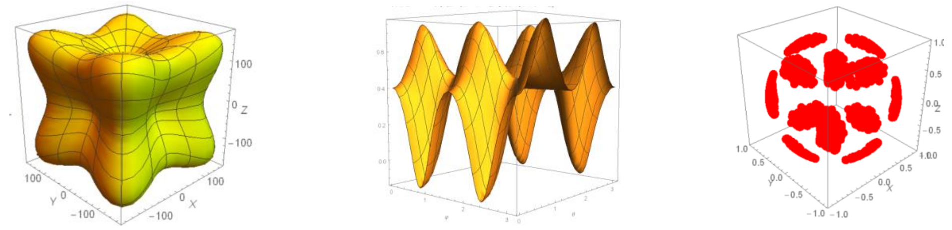
Ni 31.1% $\mu_{max}=0.77$ $\mu_{min}= -0.18 Sa=0.15$



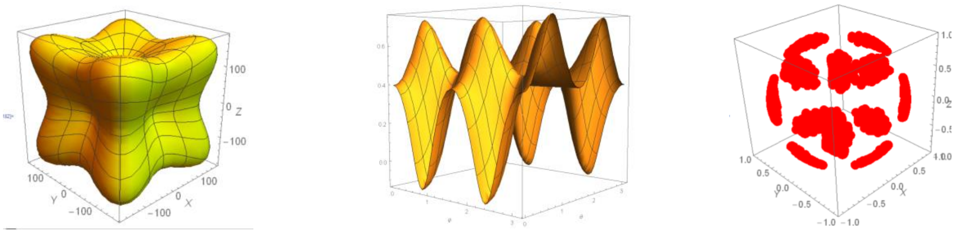
Ni 53.8% $\mu_{max}=0.75$ $\mu_{min}= -0.18 Sa=0.15$



Ni 65.5% $\mu_{max}=0.75$ $\mu_{min}= -0.18 Sa=0.15$



Ni 77.2% $\mu_{max}=0.75$ $\mu_{min}= -0.15 Sa=0.15$



Ni 92.7% $\mu_{max}=0.65$ $\mu_{min}= -0.1$ $Sa=0.11$

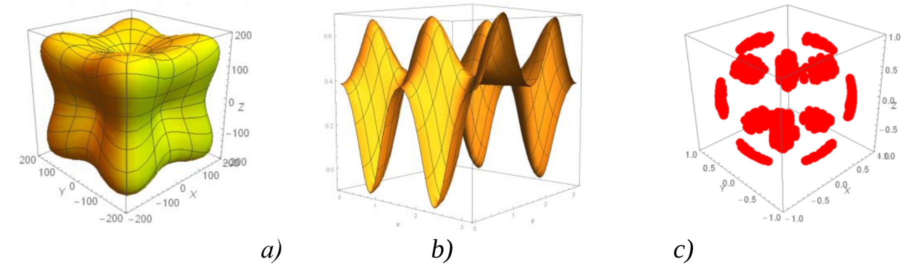


Fig.4. Characteristic surfaces of Young's moduli *(a)*, angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$ *(b)* and indicating auxeticity surfaces of single crystals *(c)* of *Cu-Ni* alloy.

This anomaly can be explained by the presence of a second-order phase transition in the pure *Ni* component (ferromagnet → paramagnet, Curie temperature $T_C = 641$ K) [11]. When cooling below T_C, ordering occurs in the arrangement of spins (magnetic phase transition of the order-disorder type or ordering type).

Such phase transformations are accompanied by a slight change in the slope of the curves of the temperature dependence of the crystal lattice periods *a(T)*. For alloys with a concentration *X = 43% Ni*, the Curie temperature decreases to *0 K* (see the state diagram of *Cu-Ni*. Fig. 1, c, page 148c [11]).

The anomalous changes in the auxetic parameters $\mu_{min}(X)$, $\mu_{max}(X)$, $S_a(X)$ that we discovered occur at a concentration of $X\approx 70\%\ Ni$ (Fig. 5, Fig. 6). It follows from the state diagram of *Cu-Ni* that for this alloy the Curie temperature is equal to room temperature, that is, the ferromagnet → paramagnet magnetic transformation occurs at $T_C=273K$. Note that the technique proposed by us makes it possible not only to reveal anomalous deformation in crystals, but also to obtain a quantitative characteristic of the auxetic properties: extreme values of Young's moduli E_{max}, E_{min}, Poisson's ratios μ_{min}, μ_{max}, and auxeticity degrees S_a of crystals under study.

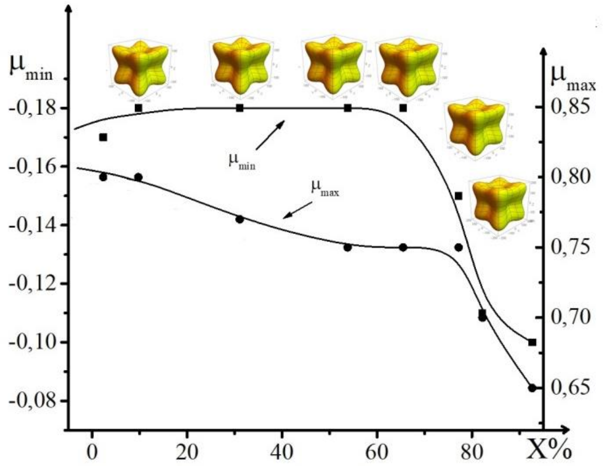


Fig.5. Dependence of Poisson's ratios μ_{max}, μ_{min} on the concentration *X* for *Cu-Ni*.

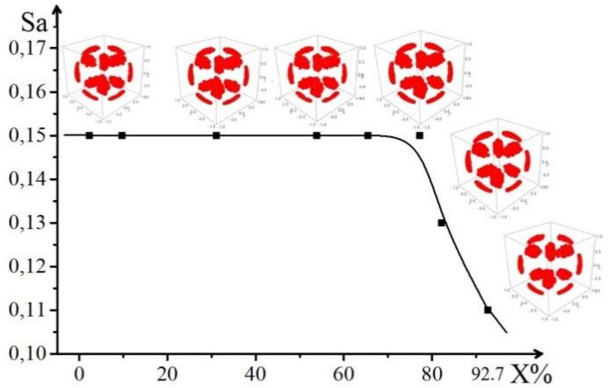


Fig.6. Dependence of auxeticity degree S_a on the concentration *X* for *Cu-Ni*.

In *Cu-Au* alloys, the components have identical *fcc* lattices. This condition is necessary but not sufficient for the formation of unlimited substitutional solid solutions. The state diagram of *Cu-Au* has a point of intersection of the liquidus and solidus curves at a temperature of 1183 K and a concentration of $X=50\%\ Au$ [1], which indicates the presence of solid state transformations in the *Cu-Au* system. Crystal lattice periods $a_{Cu}=0.361479\ nm$; $a_{Au}=0.046351\ nm$; atomic radii $r_{Au}=0.144\ nm$; $r_{Cu}=0.128\ nm$. The average deviation of the atomic radii *11 %*, which in general also satisfies the Hume-Rothery rules necessary for the formation of a continuous series of substitutional solid solutions.

Anisotropy of Young's moduli of *Cu-Au* alloys can be determined by relation (8). Thus, for instance, for an alloy with concentration $X=10\ \%$ the experimental values of Young's moduli are equal to: $E_{<100>}=62.0\ GPa$; $E_{<110>}=124.0\ GPa$; $E_{<111>}=187\ GPa$; (Fig.7), and $E_{<100>} < E_{<110>} < E_{<111>}$. The minimum values $E_{<100>}(X)$ change linearly with increasing concentration of *Au*. At the same time, anomalies are observed on the dependence curves $E_{<110>}(X)$ and $E_{<111>}(X)$ at X_1=25% and X_2=50%, which are associated with ordering processes in *Cu-Au* solid solutions, see Table 1).

Table 1

Anisotropy of Young's moduli.

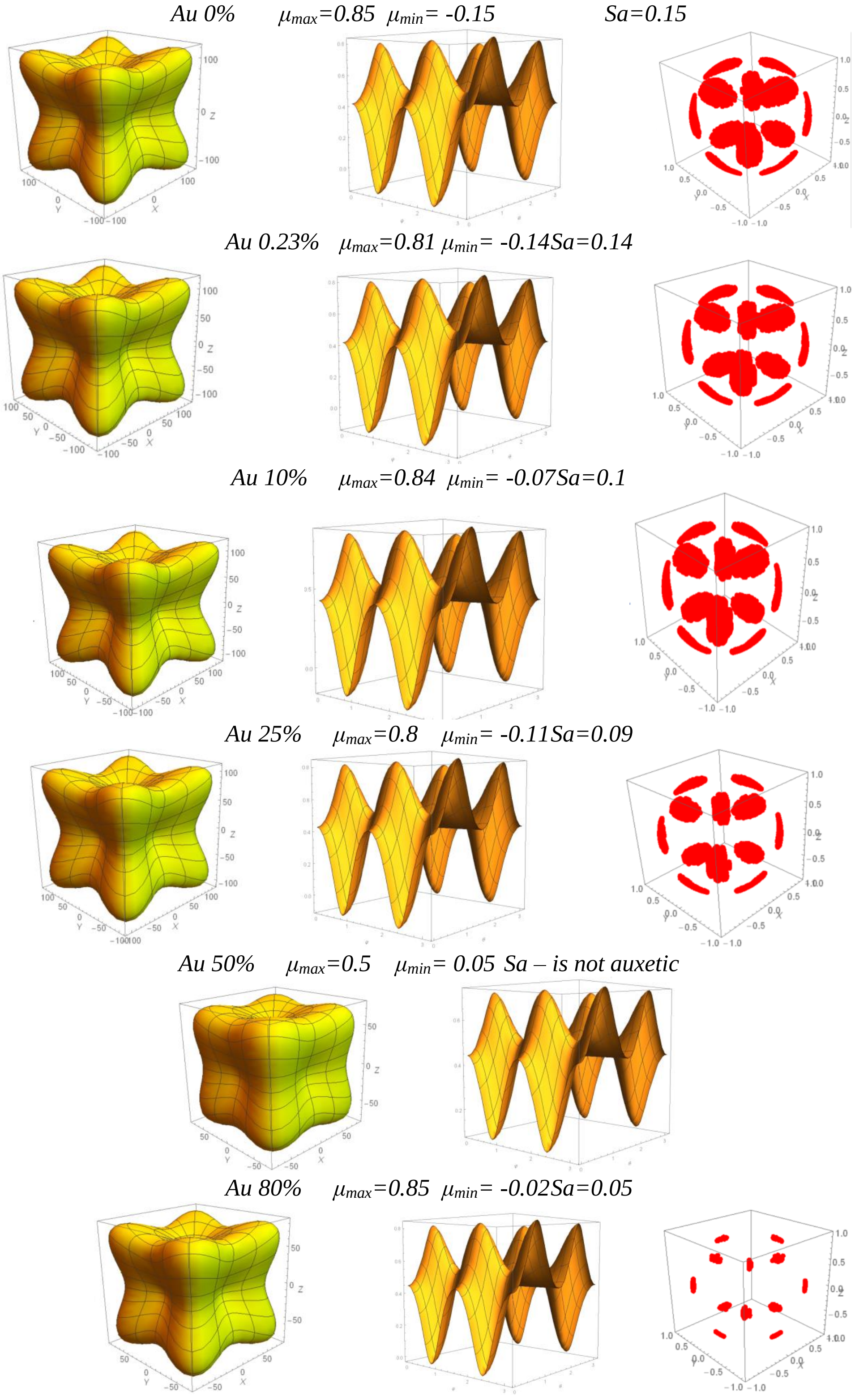
% content of *Au*	Young's moduli *E, GPa*			Shear modulus *G, GPa*
	$E_{<100>}$	$E_{<110>}$	$E_{<111>}$.	
0.23	66.4	129	189	23.4
10	62.2	125	188	21.85
25	61.5	118	171	21.5
50	54.9	90.2	114.8	19.0
80	50.8	93.6	130	17.0

Ordering phenomena in double alloys with fcc lattice are studied in detail in [1, 2, 12].

When the concentration of one of the components increases, for example, in the interval $X=(0\div 20)\ \%\ Au$, the *Cu-Au* alloy is a disordered solid solution with an fcc lattice (see the state diagram of *Cu-Au*, Fig. 1d, p. 149, [11]). The *Cu* and *Au* atoms are randomly located in the nodes of the fcc crystal lattice (Fig. 8). For an alloy of concentration $X = 25\%$, upon slow cooling from the solidus line, it is energetically favorable for *Cu* atoms to be located at the centers of 6 faces of the unit cell of the fcc lattice and the ratio between *Cu* and *Au* atoms becomes 3/1, and the formula of the chemical compound can be written as Cu_3Au. At a concentration of $X=50\%$, two more opposite faces of the fcc unit cell are occupied by *Au* atoms (see Fig. 8). Then there is one *Cu* atom per *Au* atom, and the ratio between the atoms can be written as *CuAu*. With a further increase in the *Au* concentration, the degree of ordering of the solid solutions gradually decreases until the fcc lattice of *Au* is formed. The crystal structure of ordered Cu_3Au anda *CuAu* superstructures has been repeatedly studied by X-wave and neutron diffraction methods [1, 12].

Additional information can be obtained by considering the concentration dependence of Poisson's ratio $\mu_{min}(X)$ (see Fig. 9) and the auxeticity degree $S_a(X)$ (see Fig. 10).

A slight increase in the concentration of Au (in the range of 0.23-10%) leads to the formation of disordered substitutional solid solutions and equalization of stresses in the crystal due to the chaotic arrangement of atoms. The crystal lattice period at $X=10\%$ reaches $a=0.36717\ nm$ [1]. Poisson's ratio increases from $\mu_{min}= -0.11$ to $\mu_{min}= -0.07$. Young's modulus decreases to $E_{<110>}$=125 GPa (see Table 1). With a further increase in the concentration of *Au* (from 10% to 25%), the ordering process begins, which is accompanied by a decrease in the roughness of the crystals (Young's modulus decreases from 125 GPa to 118 GPa, and Poisson's ratio μ_{min} drops from μ_{min} =-0.07 to μ_{min} =-0.11). The period of the crystal lattice increases in proportion to the increase in the concentration of *Au* and the degree of ordering, and at *X*=25% *Au* $a_{Cu3Au}=0.38199\ nm$ nm [1]. For this alloy, the



Au 0% $\mu_{max}=0.85$ $\mu_{min}=-0.15$ *Sa=0.15*

Au 0.23% $\mu_{max}=0.81$ $\mu_{min}=-0.14$*Sa=0.14*

Au 10% $\mu_{max}=0.84$ $\mu_{min}=-0.07$*Sa=0.1*

Au 25% $\mu_{max}=0.8$ $\mu_{min}=-0.11$*Sa=0.09*

Au 50% $\mu_{max}=0.5$ $\mu_{min}=0.05$ *Sa – is not auxetic*

Au 80% $\mu_{max}=0.85$ $\mu_{min}=-0.02$*Sa=0.05*

a) *b)* *c)*

Fig.7. Characteristic surfaces of Young's moduli *(a),* angular distributions of Poisson's ratios $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$ *(b)* and indicating auxeticity surfaces of single crystals *(c)* of *Cu-Au* alloys**.**

ordering temperature $T_{ord}=669$ *K*, and the auxeticity degree S_a decreases by more than an order of magnitude (from S_a =0.15 to S_a =0.09) (see Fig. 10).

An increase in the concentration of *Au* from *X=25%* to *X=50%* leads to a change in the ratio between atoms and the order of their arrangement in the fcc crystal lattice. Therefore, some of the atoms occupy well-defined places, forming superstructures, and the other part is located randomly. For a disordered alloy, the fcc lattice is preserved, and at *X=50%*, the period of the crystal lattice increases in proportion to the increase in the *Au* concentration to *a=0,39596 nm* [1], and the Young's modulus sharply decreases and reaches extremely low values $E_{<110>}=90$ *GPa* (Table 1).

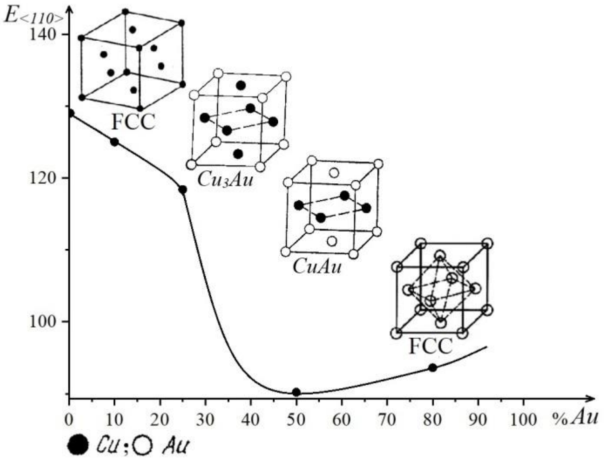


Fig.8. Concentration dependence of Young's modulus $E_{<110>}$ for *Cu-Au* alloy.

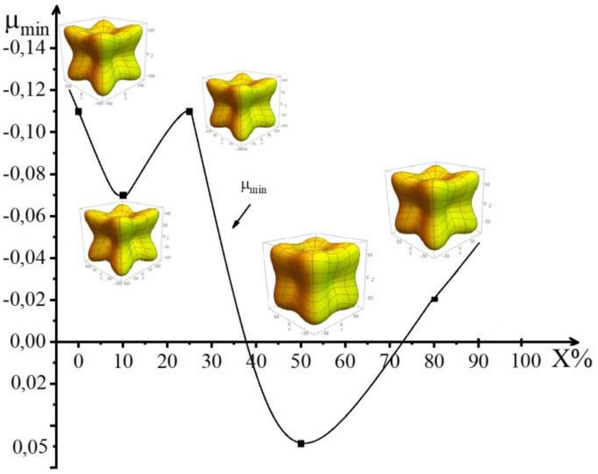


Fig.9. Concentration dependence of Poisson's ratio $\mu_{min}(X)$ for *Cu-Au* alloy.

With a slow decrease in temperature to $T_{ord} = 683\ K$, ordering and formation of *CuAu* superstructure occur for this alloy. In the [001] direction, the crystal structure of *CuAu* is formed layer by layer or consists only of a layer of *Cu* atoms or layers of *Au* atoms. As a result of the interaction between the *Cu* and *Au* layers, compression occurs and the fcc lattice turns into a tetragonal face-centered lattice with a period of *c/a* =0.935. Poisson's ratio μ_{min} increases rapidly from μ_{min} =-0.11 to μ_{min} =+0.05 and the alloy loses its auxetic properties, and the auxeticity degree S_a=0.22 (see Fig. 9, 10). Note that the redistribution of atoms in the crystal lattice and the formation of long-range order, i.e., the formation of Cu_3Au and *CuAu* superstructures, is essentially a structural phase transition of the order-disorder type, or of the ordering type. The appearance of superstructures is an additional order in the arrangement of atoms above the fcc lattice structure already existing in the alloy. Therefore, the structural phase transformation of the order–disorder type is a first-order phase transition [13].

Electronic compounds (Hume-Rothery phases)

I. Consider one of the most famous alloys *Cu-Zn* - brass. Atomic radii $r_{Cu}=0.139\ nm$, $r_{Zn}=0.128\ nm$, and their difference *(8–9)%*. The atoms of *Cu* crystallize with formation of a fcc lattice, the period of which $a=0.361479$ *nm*, and *Zn* atoms form a hexagonal close-packed (hcp) lattice with the periods a=0.26649 nm and $c=0.49469\ nm$, c/a=1.8563. The state diagram of *Cu-Zn* is given in [2, 12, 14].

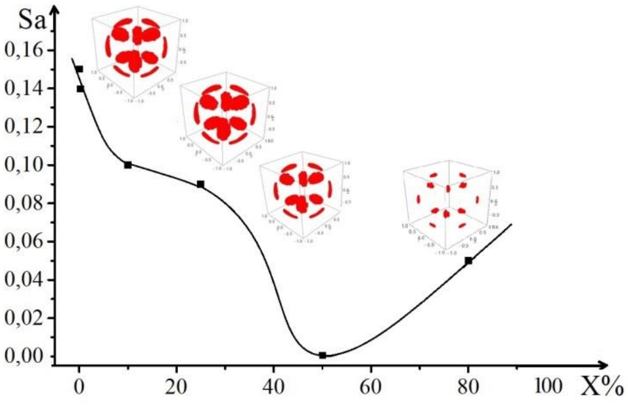


Fig.10. Dependence of auxeticity degree S_a on *X*.

In *Cu-Zn* alloys, 6 phases are formed in the solid state. In a limited α-solid solution of Zn in a crystalline fcc lattice of copper at room temperature, 39% dissolves. The stability of the fcc crystal lattice is preserved within the electron concentration n=1.98 - 1.4 (see Table 2).

Table 2

Electron concentration of some electronic compounds *Cu-Zn*.

Phase	Concentration n=e/a	Chemical formula	Lattice
A	1.98 – 1.4	Solid solution Cu(Zn)	fcc
B	1.48 – 1.5	CuZn	bcc
Γ	1.58 – 1.66	Cu_5Zn_8	complex cubic
E	1.78 – 1.87	$CuZn_3$	hcp

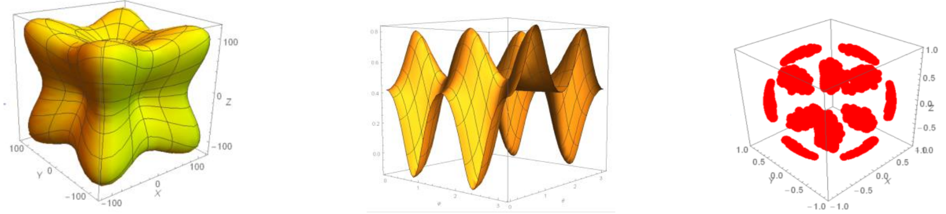
With a further increase in the electron concentration to *n=1.48–1.5*, the β-phase, which is formed on the basis of the electronic compound *CuZn* with a crystal bcc lattice, becomes stable. At high temperatures, the β-phase is a disordered solid solution. That is, the *Cu* and *Zn* atoms occupy arbitrary positions in the bcc crystal lattice. The process of ordering of atoms occurs at T_{ord} = (727–741) K.

The electronic compound Cu_5Zn_8 is formed at an electron concentration of *n=1.58–1.66* and has a complex cubic lattice with 52 atoms in the unit cell. The ordering temperature of the γ-phase is $T_{ord}=543\ K$.

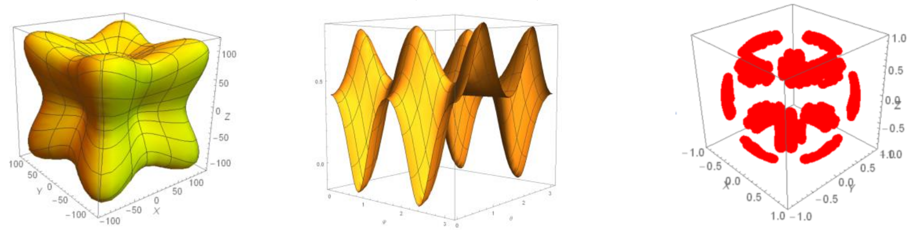
In the range of electron concentration values n = 1.78–1.87, the ε-phase is stable, i.e. the electronic compound $CuZn_3$, which has a hexagonal close-packed crystal lattice. The δ and η - phases are not electronic compounds and therefore in Table III they are not given.

The main auxetic properties of *Cu-Zn* alloys, calculated according to relations (4) – (9), are shown in Fig. 11. Most electronic compounds crystallize with the formation of cubic lattices, with the exception of ε-phases (see Table III). The regularities of the formation of the characteristic surfaces of the Young's moduli of cubic system single crystals and hcp are described in [10]. Numerical extreme values for brass $E_{<100>}$, $E_{<110>}$ and $E_{<111>}$, in a wide range of concentrations (*0÷50 %*) are given in [5]. Note the strong anisotropy of the extreme

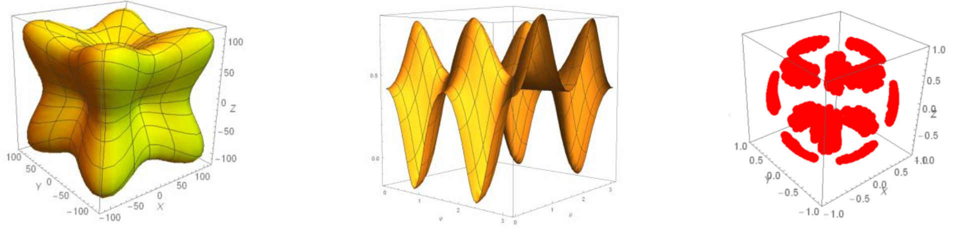
Zn 0% *α-brass* $\mu_{max}=0.85$ $\mu_{min}=-0.11$ *Sa=0.15*



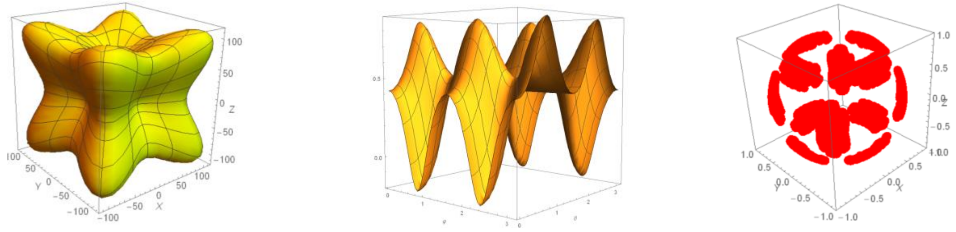
Zn 4.1% *α-brass* $\mu_{max}=0.8$ $\mu_{min}=-0.12$ *Sa=0.15*



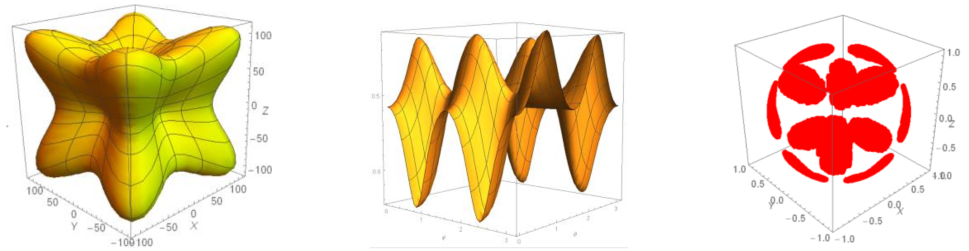
Zn 9.1% *α- brass* $\mu_{max}=0.8$ $\mu_{min}=-0.12$ *Sa=0.15*



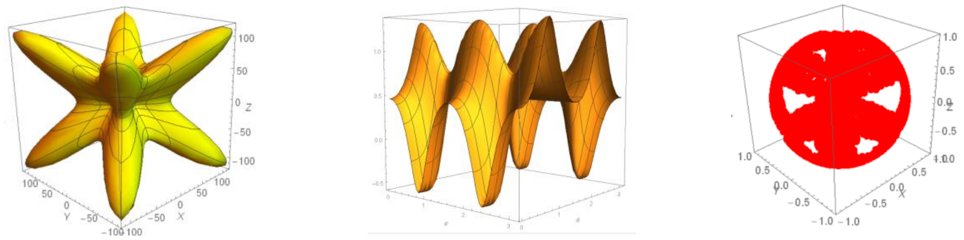
Zn 17.4 % *α- brass* $\mu_{max}=0.8$ $\mu_{min}=-0.12$ *Sa=0.18*



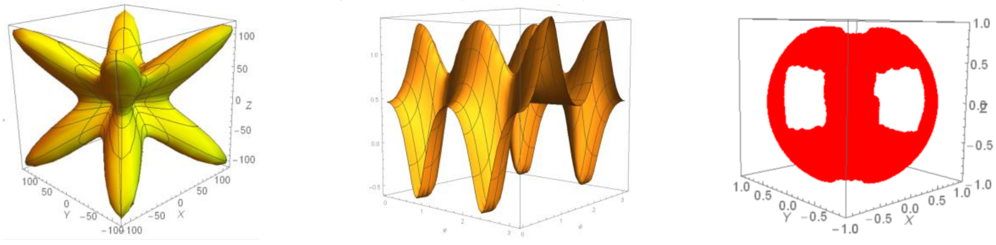
Zn 22% *α- brass* $\mu_{max}=0.85$ $\mu_{min}=-0.11$ *Sa=0.2*



Zn 45% *β- brass* $\mu_{max}=1.3$ $\mu_{min}=-0.6$ *Sa=0.4*



Zn 47.8% *β- brass* $\mu_{max}=1.3$ $\mu_{min}=-0.6$ *Sa=0.4*

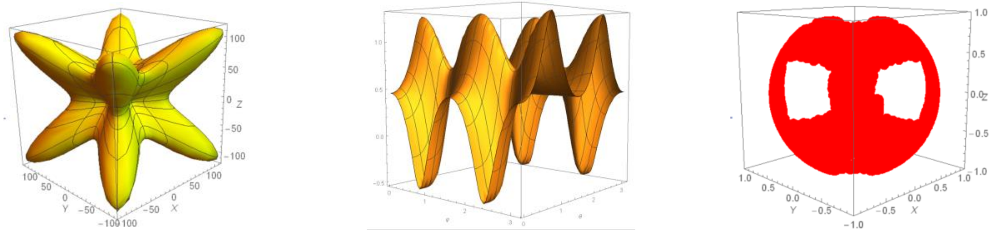


a) *b)* *c)*

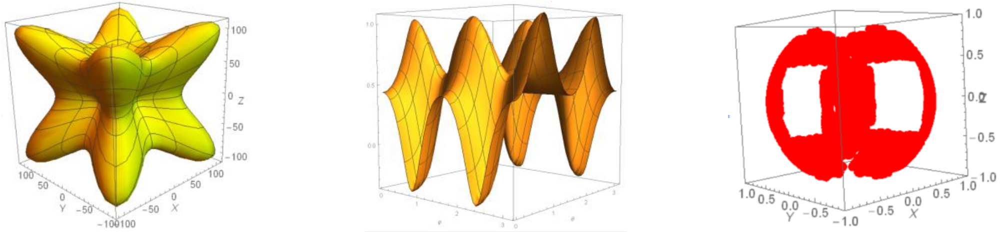
Fig. 11. Characteristic surfaces of Young's moduli *(a)*, $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$ *(b)* and indicating auxeticity surfaces of single crystals *(c)* of *Cu-Zn* alloy.

Fig. 11 (continuation)

Zn 48.8% β- brass μ_{max}*=1.31* μ_{min}*= -0.55Sa=0.39*



Zn 50% *β- brass* μ_{max}*=1.1* μ_{min}*= -0.4 Sa=0.29*



a) *b)* *c)*

Fig. 11. Characteristic surfaces of Young's moduli *(a)*, $\mu(\varphi, \Theta, \psi)$ at $\varphi=0$ *(b)* and indicating auxeticity surfaces of single crystals *(c)* of *Cu-Zn* alloy.

values $E_{<100>} < E_{<110>} < E_{<111>}$, which can change almost 7-8 times (thus, at $X=45$ % $E_{<111>}/E_{<100>}=8$).

Our calculations revealed anomalies in the dependence of the anisotropy of single crystals A(X)=2C44/(C11-C12) and Young's moduli E<hkl>(X) (see relations (5) and (6). The first anomaly is observed in the concentration interval $X_1= (39.0\div43.0)$ %. Here, the anisotropy of the crystals increases abruptly from 3.76 to 10.4, and the Young's modulus drops sharply from $E_{<110>}=115$ *GPa* to $E_{<110>}=64$ *GPa*. This is due to the phase transformation *α(fcc)→←α(fcc)+β'(bcc),* where β' is the ordered electronic compound *CuZn* (*bcc*) (see the state diagram [2, 12, 14] and Table III). Note that *α(fcc)*-brass has maximum ductility at *X* = (*35.0–39.0*) % [2].

The second anomaly occurs in the concentration interval $X_2=(46.0\div47.0)$ %, where the phase transformation *α(fcc)+β'(bcc)→←β'(bcc)* occurs and the anisotropy *A(X)* decreases from 10. 08 to 6.7, and Young's modulus increases from $E_{<110>}=$ 68.0 *GPa* to $E_{<110>}=84$ GPa. The ordered *β'(bcc)* – phase has a maximum strength of σ_B = 400 *MPa* [2].

The third anomaly is revealed during the phase transformation β'(bcc)→←β'(bcc)+γ(*complex cubic lattice*), which occurs in the concentration range $X_3=(48.8\div50.0)$ %. In this case, the anisotropy of brass single crystals decreases from *A(X)*=8.34 to *A(X)*=5.03 and Young's modulus increases abruptly from $E_{<110>}=80$ *GPa* to $E_{<110>}=96$ *GPa*. The growth of Young's modulus is caused by the appearance of a very fragile electronic compound Cu_5Zn_8 (γ-phase, see Table III). It should be noted that no anomalous dependence of Young's moduli on concentration was found for crystallographic directions $E_{<100>}$ and $E_{<111>}$.

The physical nature of the appearance of abnormal deformations can be revealed in more detail by considering the main mechanisms and regularities of formation of auxetic properties of crystals. Fig. 12 shows the concentration dependence of the negative values of Poisson's ratio $\mu_{min}(X)$ for brass in the interval $X=(0\div50)$ %.

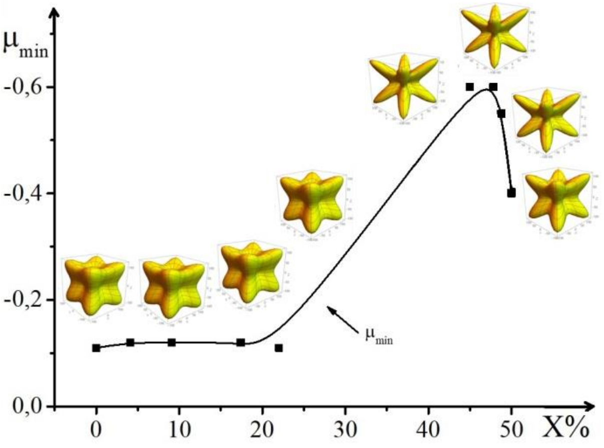


Fig.12. Dependence of Poisson's ratio $\mu_{min}(X)$ on concentration of *Zn* in brass.

In the interval *X=(0–25) % Zn*, there is a solid solution of *Zn* in the crystal lattice of *Cu(fcc)* and Poisson's ratio changes smoothly within $\mu_{min}=(-0.10)-(-0.12)$ (Fig.12). As the concentration of zinc increases from *X=25% Zn* to *39% Zn* (within the existence of substitutional solid solutions), a sharp deformation of the copper crystal lattice occurs (the difference in atomic radii *7.6 %*). The anisotropy of single crystals of *α*-brass increases rapidly (from *A*=3.21 for pure copper to *A(X)*=10.0 for a brass alloy with a concentration of *X=39%).* As shown in [14], for cubic single crystals, with an increase in the elastic anisotropy factor *A*, the negative values of Poisson's ratio μ_{min} decrease.

In this case (Fig. 12), μ_{min} decreases from μ_{min} =-(0.1–0.2) to μ_{min} =-0.6. The majority of cubic system crystals are non-axial auxetics [10], i.e. the negative values of Poisson's ratios μ_{min} are concentrated in crystallographic directions of the <110> type. Therefore, the anomalous dependence of Young's moduli should be clearly manifested only in crystallographic directions <110>.

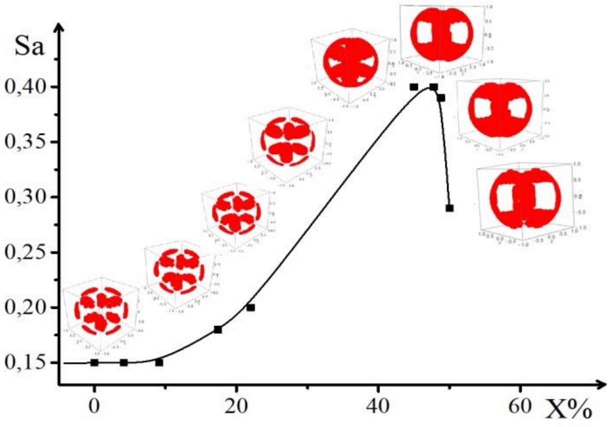


Fig.13. Auxeticity degree S_a versus concentration X of *Zn* (*α- + β- phase*).

The gradual phase transition $\alpha_{\rightarrow}{}^{\leftarrow}\alpha^{(fcc)}+\beta'(bcc)$ and $\alpha(fcc)+\beta'(bcc)\,{}_{\rightarrow}{}^{\leftarrow}\beta'$ at $X=(46.0–47.0)$ % is accompanied by a sharp increase in μ_{min} from $\mu_{min}=-0,4$ to $\mu_{min}=-0,6$. The area of indicating auxeticity surfaces S_a, increases in proportion to the increase in the elastic anisotropy factor of crystals A and to the decrease in the negative values of Poisson’s ratios μ_{min} (Fig. 13).

Conclusions

1. For the first time, characteristic surfaces of Young’s moduli, angular distributions of Poisson’s ratios μ_{min} and indicating auxeticity surfaces of *Ag-Au*, *Cu-Ni*, *Cu-Au* and *Cu-Zn* alloys were built.
2. The anisotropy of the extreme values of Young's moduli of the studied single crystals was revealed: $E_{<100>} < E_{<110>} < E_{<111>}$. An extremely high sensitivity of the $E_{<110>}$ component to auxetic phase transformations of the order-disorder type (ordering type) has been established.
3. It is shown that only a small part of the negative values of Poisson's ratios μ_{min} of these compounds is concentrated in the <110> crystallographic directions, forming auxetic properties. Therefore, the alloys under study are non-axial auxetics.
4. For *Cu-Ni* alloys, an anomaly in the concentration dependences of the auxetic parameters $\mu_{min}(X)$, $\mu_{max}(X)$ and $S_a(X)$ near the points of the second-order phase transition (ferromagnet-paramagnet) was discovered for the first time.
5. It is shown that for Ag-Au, Cu-Ni, Cu-Au and Cu-Zn alloys an increase in the auxeticity degree S_a is accompanied by a simultaneous decrease in the minimum values of the μ_{min} ratios.

Raransky M. – doctor of physical and mathematical sciences, professor of the department of information technologies and computer physics;
Oliinych-Lysiuk A. – candidate of physical and mathematical sciences, senior researcher;
Tashchuk R. – graduate student of the department of information technologies and computer physics;
Tashchuk A. – candidate of physical and mathematical sciences, teacher;
Struk A. – candidate of physical and mathematical sciences, associate professor of the department of solid state physics;
Unguryan M. – candidate of physical and mathematical sciences, teacher.

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М.Д. Раранський, А.В. Олійнич-Лисюк, Р.Ю. Тащук, О.Ю. Тащук,
А.Я. Струк, М.А Унгурян

Ауксетичні властивості деяких інтерметалічних сполук

Чернівецький національний університет імені Юрія Федьковича, м Чернівці, Україна,
m.raransky@chnu.edu.ua

Із застосуванням лінійної теорії пружності анізотропних кристалів та використанням експериментальних значень модулів пружності C_{ij} і податливостей S_{ij} наведених в таблицях Ландольт-Берштейна, вперше побудовані характерестичні поверхні модулів Юнга, кутові розподіли коефіцієнтів Пуассона $\mu(\varphi, \Theta, \psi)$ та вказівні поверхні ауксетичності монокристалів інтерметалічних сполук *Ag-Au, Cu-Ni, Cu-Au,* і *Cu-Zn*.

Встановлено надзвичайно високу чутливість складової екстремальних значень модулів Юнга $E_{<110>}$ до аномальних деформацій при фазових перетвореннях типу порядок-безпорядок. Виявлено аномалії концентраційних залежностей ауксетичних параметрів $\mu_{min}(X)$, $\mu_{max}(X)$ та ступеня ауксетичності $S_a(X)$ поблизу точок фазового перетворення другого роду типу впорядкування.

Ключові слова: Ауксетизм, модулі Юнга, коефіцієнти Пуассона, аномальні деформації, анізотропія, пружні властивості.