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The Concentration Dependences of Lattice Parameters and Debye Temperature in Multicomponent Solid Solutions

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Within both the phenomenological approximation and the framework of the principle of additivity of physical quantities of a multicomponent solid solution, including high-entropy alloys, the concentration dependences of the lattice parameter and the Debye temperature are calculated. The principle of additivity can be applied to these physical quantities, since they can be considered indirectly through the radius and mass of atoms as their own, but not collective characteristics of the individual components of the alloy. It is proposed to consider the integral and differential concentration coefficients as the quantitative measures, the values and signs of which allow us to establish the influence of each alloying element, which is represented alternately by all elements of the system, on the values of the lattice parameter and the Debye temperature. The 4–6-components' systems based on Fe, Ni, Co, Cu, Cr, Al and Ti within the equiatomic approximation are analysed.

Key words: multicomponent system, high-entropy alloys, lattice parameter, Debye temperature, principle of additivity, concentration coefficients.

У феноменологічному наближенні в рамках принципу адитивности фізичних величин багатокомпонентного твердого розчину, у тому числі й високоентропійних стопів, здійснено розрахунок концентраційних залежностей параметра ґратниці та Дебайової температури. До цих фізичних величин можна застосувати принцип адитивности, оскільки вони можуть розглядатися опосередковано через радіюс і масу атомів як власні, а не колективні характеристики окремих компонентів стопу. Запропоновано

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розглядати інтеґральний і диференціяльний концентраційні коефіцієнти як кількісні міри, величини та знаки яких уможливлюють установити вплив кожного леґувального елементу, якими виступають почергово усі елементи системи, на величини параметра ґратниці та Дебайової температури. Проаналізовано у еквіатомному наближенні 4–6-компонентні системи на основі Fe, Ni. Co, Cu, Cr, Al та Ti.

Ключові слова: багатокомпонентна система, високоентропійні стопи, параметер ґратниці, Дебайова температура, принцип адитивности, концентраційні коефіцієнти.

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1. INTRODUCTION

Theoretical and experimental research and prediction of the multicomponent and nanostructured functional-materials' properties (see, for example, Refs. [1–4]) are actual due to their wide application in various industries, electronics and medicine. In many works (see, for example, Ref. [5] and references cited therein), the concept (principle) of the additivity of physical quantities in multicomponent single-phase solid solutions (s.s.), including high-entropy alloys (HEA), is used. The essence of the additivity principle is that the average value of the physical quantity A for s.s. can be calculated according to the ratio:

$$\bar{A}_{\text{s.s.}} = \sum_{i=1}^{n} c_i A_i \,, \tag{1}$$

where c_i is the atomic fraction of element i.

Let us note that $\bar{A}_{\text{s.s.}}$ will correspond to the magnitude $A_{\text{s.s.}}$ for s.s. The idea of applying the principle was formulated in works [6, 7] in relation to the average d-orbital energy value ε_d [6] and the average value of the melting point T_{m} [7]:

$$\bar{\varepsilon}_d = \sum_{i=1}^{n} c_i \varepsilon_{d\,i} \,,\ \bar{T}_{\text{m}} = \sum_{i=1}^{n} c_i T_{\text{m}\,i} \,. \tag{2}$$

In our opinion, the principle of additivity is subject only to those quantities, which are a characteristic of atoms (for example, in the case for ε_d), but not a collective characteristic of s.s. (as in the case for T_{m}). Its own characteristics include the radius of the atom, its mass, magnetic moment, and, possibly, valence. In this case, the lattice parameter (a), Debye temperature (Θ_D), magnetic moment (μ), magnetization (M) will satisfy the additivity condition:

$$\bar{a} = a_{\text{s.s.}} = \sum_{i=1}^{n} c_i a_i,\ \bar{\Theta}_D = \Theta_D^{\text{s.s.}} = \sum_{i=1}^{n} c_i \Theta_{Di},\ \bar{\mu} = \mu_{\text{s.s.}} = \sum_{i=1}^{n} c_i \mu_i, \bar{M} = \sum_{i=1}^{n} c_i M_i \,. \tag{3}$$

If the condition of equality of valence in the isolated atom and the s.s. atom is fulfilled, then, we can write the ratio for the specific resistance similar to Eq. (3):

$$\overline{\rho} = \rho_{\text{s.s.}} \cong \sum_{i=1}^{n} c_i \rho_i \ . \tag{4}$$

Because ρ_i can be represented as $\rho_I = C_i/(n_i\lambda_{0i})$, where C_i is proportionality factor, n_i and λ_{0i} are the concentration and the average free path of electrons, Eq. (4) will be the approximation only, and, it can be extended to the cases of the thermal-resistance coefficient $\overline{\beta} = \beta_{\text{s.s.}} = d\ln\rho_{\text{s.s.}} / dT$ and the longitudinal-strain coefficient $\overline{\gamma}_1 = \gamma_1^{\text{s.s.}} = d\ln\rho_{\text{s.s.}} / d\varepsilon_1$ ($d\varepsilon_1$ is longitudinal strain) as approximate too. The degree of approximation depends on the difference $(\lambda_{0i} - \lambda_{0i}^{\text{s.s.}})$.

Taking into account this one, we calculated the concentration dependence of the lattice parameter and the Debye temperature [5]. Based on these data, their concentration coefficients were calculated for 4–6-components' s.s. that was the goal of this work.

Note that the integral and differential concentration coefficients are more sensitive to changes in the elements' concentration compared to the concentration dependences of the lattice parameter and the Debye temperature. This opens the possibility to follow the change of these values in more detail.

2. METHODS OF CALCULATING INTEGRAL AND DIFFERENTIAL CONCENTRATION COEFFICIENTS OF SOLID SOLUTIONS

Concentration dependences were obtained on the basis of the ratios:

$$\overline{a} = a_{\text{s.s.}} = \frac{1-x}{n-1}\sum_{i=1}^{n-1} a_i + x a_n \ , \ \overline{\Theta}_D = \Theta_D^{\text{s.s.}} = \frac{1-x}{n-1}\sum_{i=1}^{n-1}\Theta_D + x\Theta_{Dn} \ , \tag{5}$$

where the multiplier $(1-x)/(n-1)$ indicates the equiatomicity of the s.s. at a given atomic fraction of the doping (under number n) element, which, for convenience, we denoted by x.

The concentration integral (denoted by the index 'i') and differential (with index 'd') coefficients were calculated based on the standard ratios:

$$(\beta_a(x_i))_{\text{i}} = \frac{1}{a(0)}\frac{a(x_i)-a(0)}{(x_i-0)}, \ (\beta_{\Theta_{\text{D}}}(x_i))_{\text{i}} = \frac{1}{\Theta_{\text{D}}(0)}\frac{\Theta_{\text{D}}(x_i)-\Theta_{\text{D}}(0)}{(x_i-0)},$$

$$(\beta_a(x_{i+1}))_{\text{d}} = \frac{1}{a(x_i)}\frac{a(x_{i+1})-a(x_i)}{(x_{i+1}-x_i)}, \ (\beta_{\Theta_D}(x_{i+1}))_{\text{d}} = \frac{1}{\Theta_D(x_i)}\frac{\Theta_D(x_{i+1})-\Theta_D(x_i)}{(x_{i+1}-x_i)}, \tag{6}$$

where $a(0)$ and $\Theta_D(0)$ correspond to the lattice parameter and Debye temperature s.s. at the concentration of the doped element $x = 0$, indices 'i' and '$i+1$' number the concentration intervals.

Figures 1–3 present the results of calculations based on ratios (4) and (5) for four- and six-component systems based on Fe, Ni, Co, and Cu; Fe, Ni, Co, Cu, Cr and Ti, respectively. Note that we obtained similar results for the case of a five-component system based on Fe, Ni, Co, Cu, and Al (data on the concentration dependence of the lattice parameter and the Debye temperature are given in [4]).

3. ANALYSIS OF RESULTS

We note the following. Figure 1, *a* shows the point of intersection of the concentration curves at the concentration x_e, which we called equi-

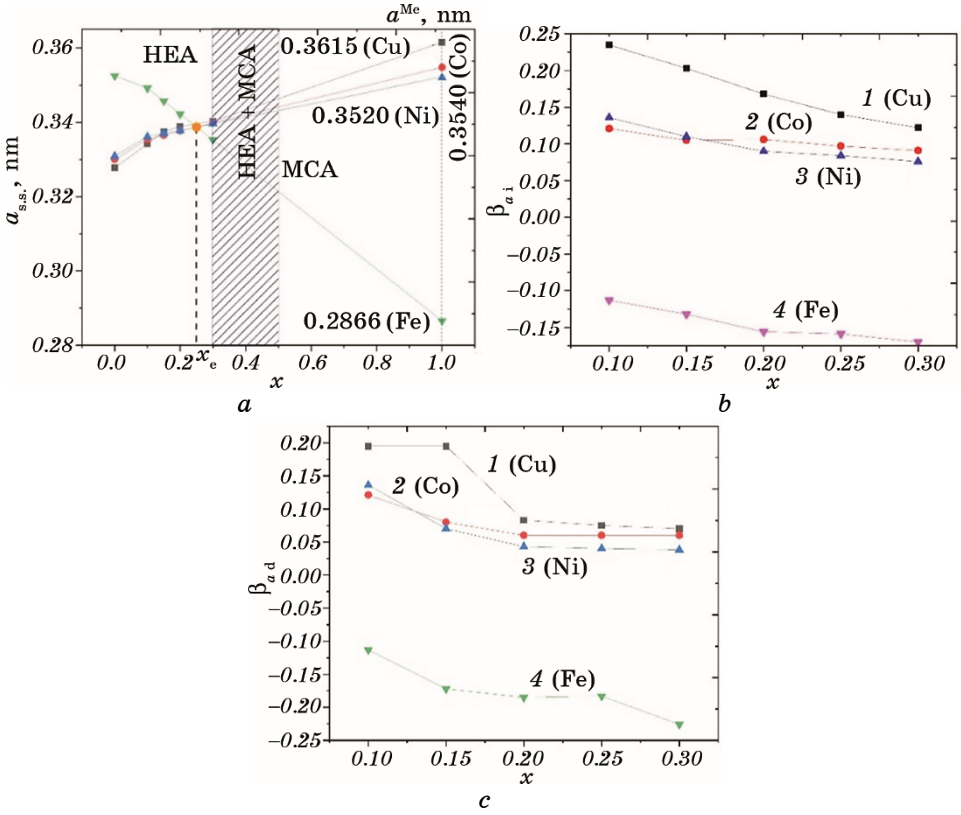

Fig. 1. The concentration dependences of the lattice parameter (*a*), integral (*b*) and differential (*c*) concentration coefficients for the four-component s.s. MCA–multicomponent alloy. The shaded area at position *a* is the hypothetical concentration interval where HEA + MCA is observed.

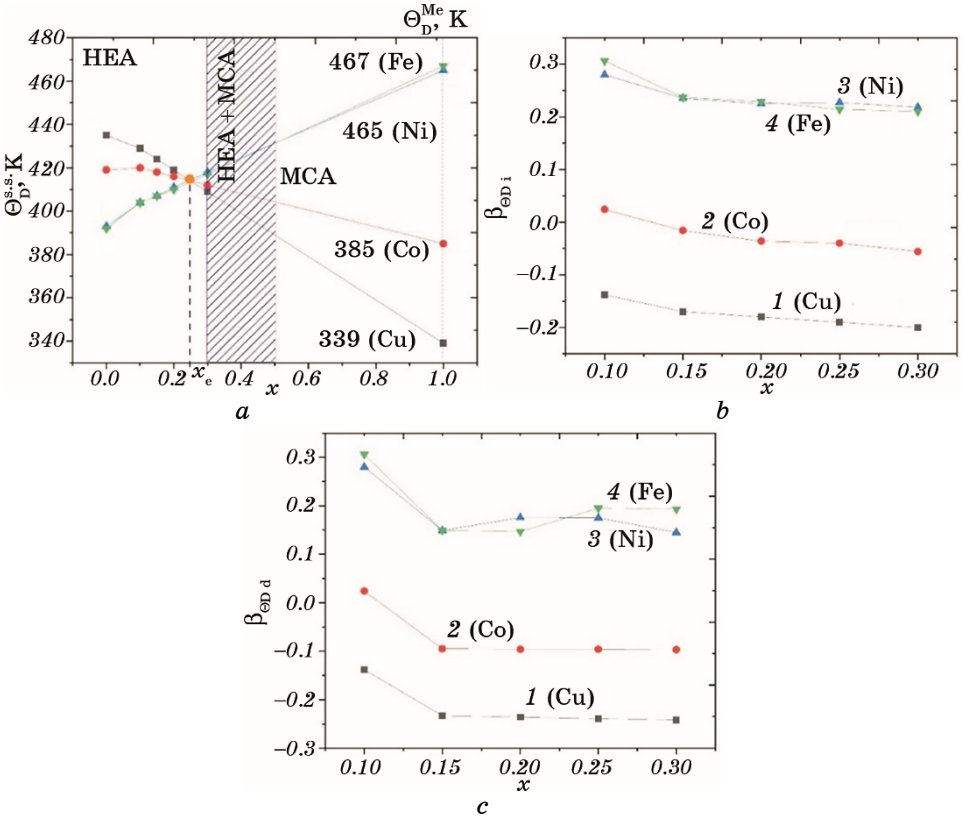

Fig. 2. The concentration dependence of the Debye temperature (*a*), integral (*b*) and differential (*c*) concentration coefficients for the four-components' s.s.

librium. Its peculiarity is that, at a given the atomic fraction, as expected for an equiatomic alloy, the lattice parameters, as well as the Debye temperature, have a constant value regardless of the supporting element, which is indicated in brackets in the right half of each position.

On the example of four-, five-, and six-component systems, a simple rule $x_e = n - 1$ was established. It follows from Fig. 1, *a*, by changing the concentration of the doped element (it appears in our case under the number n), it is possible to vary the lattice parameter within wide limits ($\Delta a = 0.2$ nm). We will also point out that the values of the integral concentration coefficient as averaged over the entire interval x and the differential concentration coefficient as a function of the point differ slightly in magnitude, but not in sign. The negative the coefficients value indicates that an increase in the Fe atoms concentration

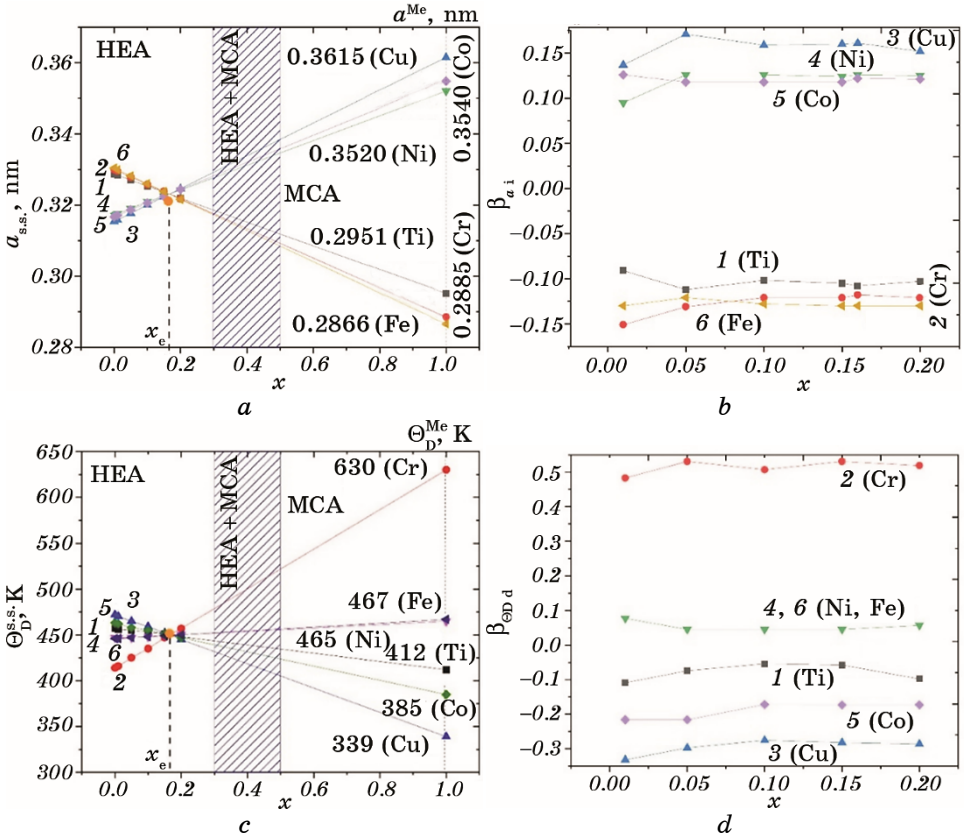

Fig. 3. The concentration dependence of the lattice parameter (*a*), Debye temperature (*c*), and the corresponding integral concentration coefficients (*b*, *d*) for the six-component system.

causes the lattice parameters to decrease in the s.s. In many respects, a similar situation is observed when analysing the concentration dependence of the Debye temperature (Fig. 2).

Thus, in the concentrations interval $x = (0 - x_e)$, in which the HEA is realized, the $\Delta\Theta_D^{s.s.} = 45$ K, the values can be varied $\Theta_D^{s.s.}$. At the same time, doping elements Cu and Co cause its decrease. We emphasize once again that at x_e the Debye temperature has a constant value regardless of the doped element. On the Figure 3 presents the results of calculations of the concentration dependence of the lattice parameter, the Debye temperature, and the integral concentration coefficient for the six-component system.

Note that we did not present the data for the differential concentration coefficient, since its values are very close to the integral coefficient value with a similar functional dependence (the situation is simi-

lar to Fig. 2, *b*, *c*). Figure 3, *b* attracts attention, in which two groups of elements Cu, Ni, Co and Ti, Cr, Fe provide a positive or negative of the concentration coefficient.

4. CONCLUSION

At the phenomenological level, calculations based on data [8, 9] and analysis of the concentration dependence of dynamic parameters such as lattice parameter and Debye temperature, for which the additivity principle of physical quantities in multicomponent systems solid solutions is fulfilled, including high-entropy alloys, were made.

It was concluded that the principle of additivity is fulfilled only in the case when the physical quantity is its own and not a collective characteristic of atoms.

Eigenvalues include the size and mass of atoms. The melting temperature, mean free path of electrons, resistivity, etc. are collective properties of multicomponent materials. In this regard, in the case of electrophysical properties (resistivity, thermal resistance coefficient, strain coefficient [5] or melting point [7, 10]) the additivity principle can be used only approximately. As a measure of the quantitative characteristics of the influence of the concentration of the doping element on the lattice parameter and the Debye temperature, we determined the integral and differential concentration coefficients. The magnitude and sign of these coefficients provide information about the nature of the effect of one or another doping element on the lattice parameter and the Debye temperature in solid solutions.

Finally, we note that our choice of multicomponent systems was based on studies of physical properties (coercivity, magnetization, thermal diffusion) [11] and phase composition [12] of HEA based on Fe, Co, Ni, Cu, Cr, Al, and Ti. This made it possible to more correctly formulate the tasks of our research.

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