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Concentration effects in multicomponent metallic solid solutions

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In the equiatomic approximation, the dependence of the lattice FCC parameter and the Debye temperature from the atomic fate x of the doping element, which is alternately represented by all elements of a multicomponent solid solution, including high-entropy alloys were obtained. The calculations were carried out on the example of a five-component (based on Cu, Ni, Co, Fe, and Al) or six-component (based on Cu, Ni, Co, Fe, and Cr, Ti) metal systems. It was found that by varying x within $x = (0 - 0.3)$, it is possible to obtain a change in the lattice FCC parameter from 0 to 0.03 nm and the Debye temperatures from 0 to 80 K. The proposed new characteristics are integral and differential concentration coefficients, the magnitude and sign of which can predict concentration dependences for the lattice parameter and the Debye temperature.

Keywords: Lattice parameter; Debye temperature; Multicomponent and high-entropy solid solution; Equiatomic approximation; Concentration coefficients.

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Introduction

The authors [1-3] attempted to apply the principle of additivity of physical quantities (average d-orbital energy and melting temperature) in their calculations in the case of high-entropy alloys (HEA). The work [4] also analyzed the issue of the possibility and limits of applying the principle of additivity to physical properties (for example, specific resistance, strain sensitivity, magnetization, etc.) or characteristics (for example, the atom magnetic moment, melting temperature, lattice parameter, Debye temperature and etc.) in the case of multicomponent metallic solid solutions (s.s.), including high-entropy ones. It was concluded that calculations of physical quantities or characteristics using the principle of additivity, which can be presented in the following form:

$$A = \sum_{i=1}^n c_i \cdot A_i, \quad (1)$$

where i - is a component number and its atomic fraction (c_i); A and A_i – the value of a physical quantity or characteristic for s.s. or i components respectively, can claim accuracy if A_i represent the own characteristics of atoms (their size, mass, magnetic moment, etc.).

From this point of view, such dynamic characteristics

as the s.s. lattice parameter and the Debye temperature, magnetization, valence of atoms can be indirectly interpreted as their own characteristics, and for their prediction (calculations) you can use relation (1).

In the case of the thermal resistance coefficient and the strain coefficient:

$$\beta_T = \frac{d \ln \rho(T)}{dT} \quad \text{and} \quad \gamma_l = \frac{d \ln R}{d \varepsilon_l} = \frac{d \ln \rho(\varepsilon_l)}{d \varepsilon_l} + 1 + 2\mu_f, \quad (2)$$

where ρ is resistivity; R – resistance; ε_l – longitudinal deformation; μ_f – Poisson's ratio, relations $\frac{d \rho}{\rho(T)}$ and $\frac{d \rho}{\rho(\varepsilon_l)}$ with a certain degree of convention, they can also be considered as their own characteristics and prognosis β_T and γ_l lead within the framework of relation (1). At the same time, such physical quantities as resistivity (ρ), mean free path of electrons (λ_0), melting point (T_m), Fermi energy (ε_F) have a collective character and cannot be predicted using relation (1), although experimentally determined values λ_0 and ρ HEA films [5] well correspond to the calculated ones. This can be explained by the fact that the experimental values were obtained on the example of film HEAs with a random ratio of components, and the calculations were carried out for the case of an equiatomic composition of bulk crystals, and the indicated

coincidence may be situational.

In the case of the lattice parameter fcc s.s. ($a = 0.360 - 0.365$ nm) [6] a very good correspondence of experimental and calculated results is observed. It should also be noted that the physical properties of film HEAs have been studied quite widely in the last decade (see, for example, [7- 10]), but, all the same, not enough concrete results have been obtained for comparison with calculated ones. For this reason, we were able to compare calculations and experimental results only in the case [5, 6].

I. Methodology of calculations, working ratios

For lattice parameter calculations (a) and Debye temperatures (θ_D) s.s. depending on atomic fraction (x) doping element (n -element) obvious ratios were used:

$$a = \sum_{i=1}^{n-1} c_i a_i + x a_n, \quad \theta_D = \sum_{i=1}^{n-1} c_i \theta_{Di} + x \theta_{Dn} \quad (3)$$

in the case of arbitrary atomic fractions (concentrations) of ($n-1$) elements or

$$a = \frac{1-x}{n-1} \sum_{i=1}^{n-1} a_i + x a_n, \\ \theta_D = \frac{1-x}{n-1} \sum_{i=1}^{n-1} \theta_{Di} + x \theta_{Dn} \quad (4)$$

in the case of equiatomic composition ($n-1$) components that act as phase-forming. It should be noted that, for convenience, we denote the atomic fraction of the doping element by the symbol x .

Note that there is no fundamental difference between (3) and (4), but relations (4) are more convenient.

Typical dependencies $a_{s.s.}(x)$ and $\theta_D^{s.s.}(x)$ presented in Fig. 1. When receiving them, we used data about a and θ_D , presented in the academic directory [10, 11]. Let's note their characteristic features.

First of all, at a certain equiatomic atomic fraction he for all five elements, they all intersect at a certain point, which can be interpreted as the realization of the equilibrium state s.s. Secondly, by changing the doping

element (and all n elements appear alternately), we can vary both $\theta_D^{s.s.}$ and $a_{s.s.}$ within wide limits. This opens up the possibility of changing the phonon spectrum, which may allow offering a sensitive element of one of the acoustoelectronic sensors. As for the lattice parameter, in this case we are not talking about the practical application of the effect of varying the parameter $a_{s.s.}$.

Finally, extrapolation $a_{s.s.}(x)$ and $\theta_D^{s.s.}(x)$ at the $x = 1$ allows you to at least approximate the behavior of these characteristics in multicomponent alloys (MCA). We will also note the following detail of our calculations in the case of a metallic system, one of which is a component Ti with HCP (low temperature phase) or BCC (high temperature phase) lattices We made calculations using the value a_{HCP} , assuming that the Ti atoms occupy their specific positions in the FCC lattice s.s. Along with this, in the case of Co, we used the value of the parameter FCC Co as a high-temperature phase. Sensing some incorrectness of various approaches in the case of hexagonal Ti and Co, we made a calculation using the value of the virtual parameter FCC phases Ti, which was calculated according to a known ratio $a_{FCC} = \sqrt{2} \cdot a_{HCP}$ (see section 3).

Analyzing the data on Fig. 1, we come to the conclusion that they must be supplemented with the dependence of the so-called concentration coefficients on the atomic fraction x . We denote the integral and differential concentration coefficients by indices « i » and « d » means as follows:

$$(\beta_a(x_i))_i = \frac{1}{\alpha(0)} \cdot \frac{\alpha(x_i) - \alpha(0)}{(x_i - 0)}, \\ (\beta_{\theta_D}(x_i))_i = \frac{1}{\theta_D(0)} \cdot \frac{\theta_D(x_i) - \theta_D(0)}{(x_i - 0)}, \\ (\beta_a(x_{i+1}))_d = \frac{1}{\alpha(x_i)} \cdot \frac{\alpha(x_{i+1}) - \alpha(x_i)}{(x_{i+1} - x_i)}, \\ (\beta_{\theta_D}(x_{i+1}))_d = \frac{1}{\theta_D(x_i)} \cdot \frac{\theta_D(x_{i+1}) - \theta_D(x_i)}{(x_{i+1} - x_i)}, \quad (5)$$

indices « i » and « $(i+1)$ » concentration intervals are numbered. This is implemented on the example of a six-component system (Fig. 2).

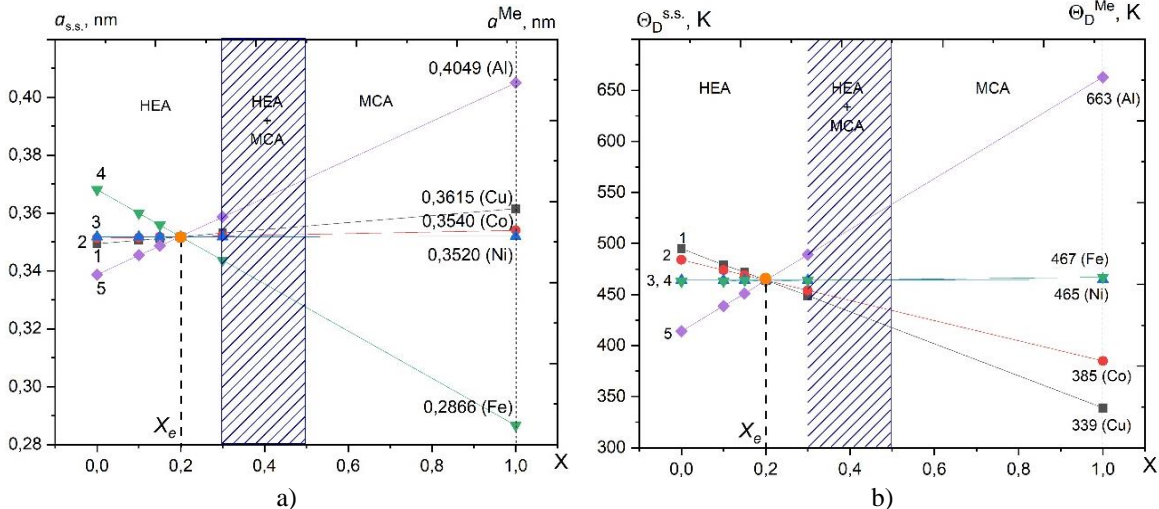


Fig. 1. Concentration dependence of the lattice parameter (a) and the Debye temperature on x (b) for bulk samples of the five-component system (HEA) based on Cu, Ni, Co, Fe, and Al. MCA is a multi-component alloy.

II. Concentration coefficients of the lattice parameter and the Debye temperature

In fig. 2 presents calculated dependencies $a_{s.s.}$ and $\theta_D^{s.s.}$ from the atomic fraction x of the doping element for the six-component system for bulk samples; dependencies are also presented here $(\beta_a)_d$ and $(\beta_{\theta_D})_d$ from x . Based on these data, the following features of the presented dependencies can be indicated.

In the case of $a_{s.s.}(x)$, as expected, the dependences are linear regardless of the nature of the doping element, since in the HEA the atomic radii satisfy the high-entropy condition. At the same time linear character $\theta_D^{s.s.}$ is optional and is most likely implemented in the case of close values $\theta_D^{s.s.}$ for individual components.

We will also point out that the use of the virtual phase lattice parameter in the calculations Ti $a_{FCC} = 0.4160$ nm does not lead to fundamentally new results, since the linear dependence is preserved $a_{s.s.}(x)$, but the equilibrium point shifts to a magnitude $a_{s.s.} = 0.3425$ nm and the slope changes its negative value to a positive one. Thus, the question of the correctness of

use in calculating the value a_{HCP} hexagonal or a_{FCC} of the virtual Ti phase remains open to a large extent.

With regard to concentration coefficients, then with linear dependencies $a_{s.s.}(x)$ and $\theta_D^{s.s.}(x)$ they will have a constant value at each doping element. Their negative value will be associated with a decrease $a_{s.s.}$ and $\theta_D^{s.s.}$ with an increase in the value of x for certain doping elements, and a positive value - on the contrary, will be associated with an increase in these characteristics. Thus, the magnitude and sign of the concentration coefficients allow us to qualitatively predict the nature of the change $a_{s.s.}$ and $\theta_D^{s.s.}$ when varying the atomic fraction of doping elements.

Conclusions

In the equiatomic approximation, the dependence of the lattice parameter was calculated $a_{s.s.}$ and temperature Debye $\theta_D^{s.s.}$ from the atomic fraction of the doping element x , which alternately acts as one of the components of the five-component (based on Cu, Ni, Co, Fe i Al) or six-component (based on Cu, Ni, Co, Fe and Cr, Ti) multicomponent bulk s.s., including high entropy (HEA). Based on these results, the dependences of the integral and

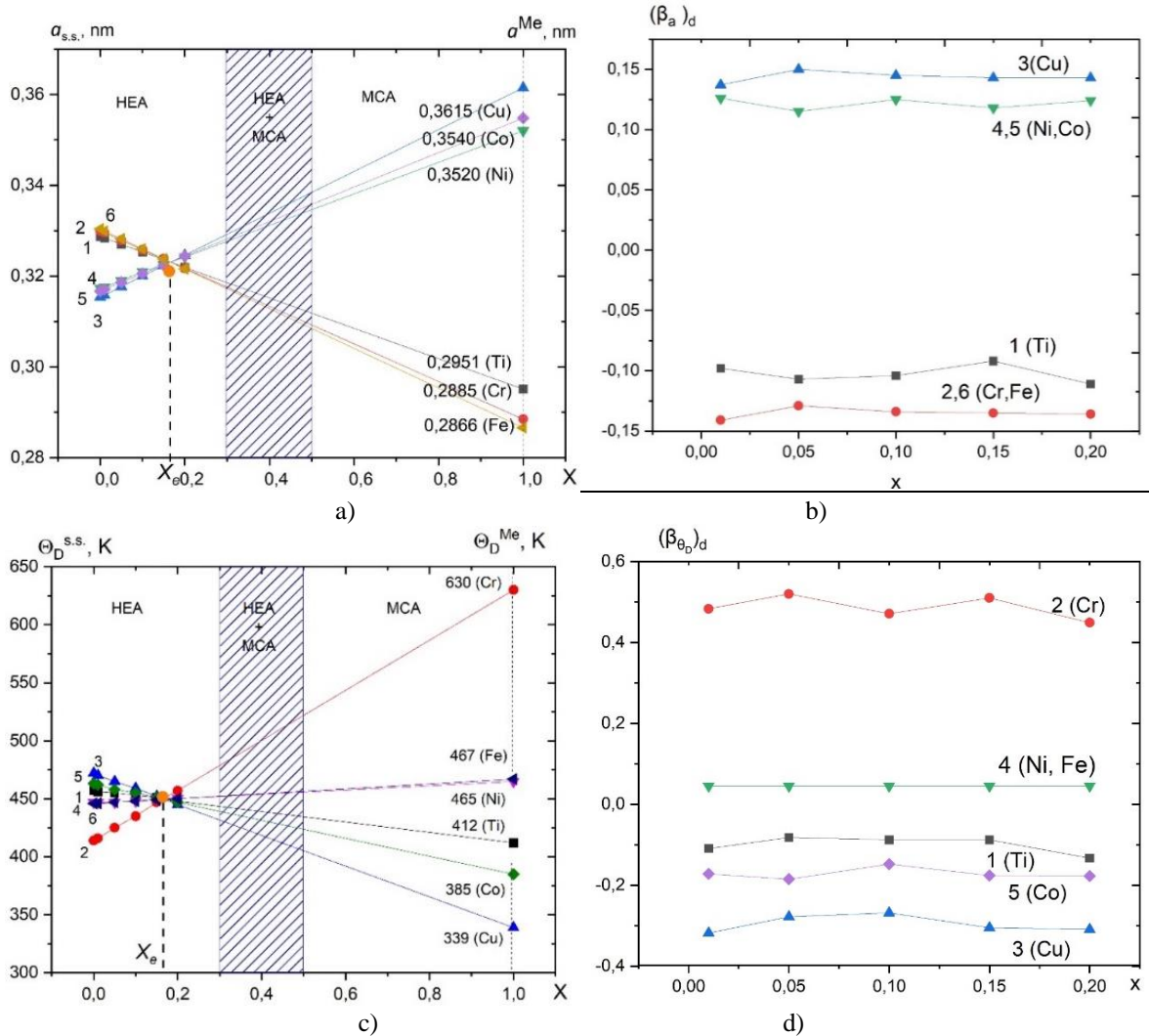


Fig. 2. Concentration dependence of the lattice parameter (a), Debye temperature (c), and differential concentration coefficients (b, d), respectively, for a six-component system based on Cu, Ni, Co, Fe, Cr i Ti. MCA – multicomponent alloy.

differential concentration coefficients, which are proposed for consideration for the first time, were calculated. Because dependencies $a_{s,s.}$ and $\theta_D^{s.s.}$ from x have a linear character, then the concentration coefficients for each doping element practically do not depend on x , in contrast to their magnitude and sign. Using concentration coefficients, it is possible to predict values $a_{s,s.}$ and $\theta_D^{s.s.}$.

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Концентраційні ефекти в багатокомпонентних металевих твердих розчинах

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В еквіатомному наближенні отримано залежність ГЦК-параметра ґратки та температури Дебая від атомної доли x легуючого елемента, який по черзі представлений усіма елементами багатокомпонентного твердого розчину, в тому числі високоентропійними сплавами. Розрахунки проводились на прикладі п'ятикомпонентної (на основі Cu, Ni, Co, Fe та Al) або шестикомпонентної (на основі Cu, Ni, Co, Fe та Cr, Ti) металевих систем. Встановлено, що змінюючи x в межах $x = (0 - 0,3)$, можна отримати зміну параметра ГЦК ґратки від 0 до 0,03 нм і температур Дебая від 0 до 80 К. Нові характеристики, що були запропоновані, є інтегральними і диференціальними коефіцієнтами концентрації. За їх величиною і знаком можна передбачити концентраційні залежності для параметра решітки і температури Дебая.

Ключові слова: Параметр ґратки; температура Дебая; багатокомпонентні і високоентропійні тверді розчини; еквіатомне наближення; концентраційні коефіцієнти.