

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

Thermodynamic Investigations on the Component Dependences of High-entropy Alloys¹

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Abstract—In the present research, a study on the thermodynamical properties of the quinary Co–Cu–Cr–Fe–Ni high-entropy alloys and ternary Ca–Sb–Yb is carried out by the models Kohler, Chou’s general solution method (GSM) and Muggianu. The dependences of composition variation on thermodynamic properties, such as enthalpy of mixing of Co–Cu–Cr–Fe–Ni alloys in simple FCC phase are investigated at the temperatures 1273, 1373, and 1473 K. Moreover, a comparison between the results of the three models and those of other theoretical models shows good mutual agreement.

Keywords: geometrical model, Redlich–Kister coefficients, mixing enthalpy, high-entropy alloys

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INTRODUCTION

Traditionally, the field of materials science and engineering has predominately focused on processing materials, establishing structure–property relations and measuring material properties. Particularly in the last few decades, this empirical approach is increasingly shifting toward the design of materials to achieve optimal functionality, driven by advances in computational materials science and information technology. Scientists are nowadays witnessing a paradigm shift in materials research and development from experimental based knowledge creation to integrated computational–prediction and experimental validation approaches. Thermodynamic properties of alloys can generally be obtained by experimental measurements. However, it is not always possible to perform experimental measurement for multicomponent alloys due to technological difficulties, expenses and time consumption. A necessity of handling thermodynamic data on multicomponent systems has arisen nearly several decades ago and still remains a topical problem. Thermodynamics, a key component of materials science and engineering, is typically represented by phase diagrams traditionally for binary and ternary systems. Consequently, the applications of thermody-

namics have been rather limited in multicomponent engineering materials.

For thousands of years, the development and production of alloys are basically dominated by one primary metallic element, through adding appropriate amount of alloying elements to adjust and improve alloy’s physical and chemical properties to meet different application requirements. Yeh et al. proposed the idea of multiprinciple element alloys and successfully synthesized a series of new alloys including five to eight elements in equimolar quantities in the mid-nineties of the last century [1, 2]. These new alloys are called high-entropy alloys (HEAs). HEAs have many exceptional properties, such as strong work-hardening capacity, wear resistance, very high mechanical strengths and satisfied oxidation resistance. It is expected that these high-entropy alloys will eventually replace the traditional alloys as main structure materials in future. Since the first report of HEA, some extensive experimental works related to alloy design and processing have been done all over the world [3–6]. Nevertheless, because of the great complexity of structure modeling of alloys, the present situation for the theoretical investigation on HEAs in question is still far from satisfactory.

To meet the requirement of thermodynamic data, modeling the thermodynamic of complex HEAs has attracted many scientists’ attention over the past decades [7–12].

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There are various methods of processing thermodynamical data and performing thermodynamic calculations in the case of multicomponent systems. To all appearances, the Calphad method is still the most widely used one.

Computational thermodynamics, based on the Calphad approach, developed in the last few decades, has released the power of thermodynamics and enabled scientists and engineers to make phase stability calculations routinely for technologically important engineering materials. On the other hand, geometric models give the possibility to predict the thermodynamic properties of multicomponent alloys using data that belongs to respective binary order systems.

Since the 1960s, dozens of models, which are used to calculate the thermodynamic properties, have been proposed. The enthalpy of formation as the leading term of Gibbs free energy, is an important parameter in alloy development because of its strong influence on phase equilibria in an alloy system. Thus, a relatively simple model in order to calculate the enthalpy of mixing is employed in this study that may be demanded in conditions of severe shortage of thermodynamic data concerning subsystems of the system studied, just up to the binary subsystems.

In the present study, three different thermodynamic prediction methods, such as GSM [13], Kohler's method [14], and the Muggianu method [15] having symmetric property, were used in order to calculate the enthalpy of mixing of ternary and quinary fcc alloys having low entropy Ca–Sb–Yb and Co–Cu–Cr–Fe–Ni solid alloys having HEAs. The calculated results are compared with those obtained from first principle calculation and theoretical ones [16–26].

LITERATURE SURVEY

Several theoretical investigations of the enthalpy of mixing of solid alloys can be found in the literature:

Formation condition of high-entropy alloys with solid solution structure was investigated. Seventeen kinds of the HEAs with different components were prepared, the influencing factors (the comprehensive atomic radius difference δ , the mixing enthalpy ΔH and the mixing entropy ΔS) of phase composition of the alloys were calculated and the microstructure and phase compositions of alloys were analyzed by using SEM and XRD. In this study, it is found that only the systems with $\delta \leq 2.77$ and $\Delta H \geq -8.8$ kJ/mol will form high entropy alloys with simple solid solution, otherwise, intermetallic compounds would exist in these alloys and the selection of the type of element has important effects on microstructure and properties of high entropy alloys [26].

It is shown by Li and Zhang that the Gibbs free energy of mixing of the equimolar Al–Cr–Fe–Ni–Cu alloy is smaller than that of inter-metallic compounds. Moreover, the crystal structures of the cast Al–Cr–

Fe–Ni–Cu alloy are characterized and only simple solid-solution structures, especially fcc and bcc, are identified from the XRD analyses, but intermetallic compounds do not appear [27].

Park et al. [21] studied the re-crystallization behaviors of conventionally cold-rolled Co–Cr–Cu–Fe–Ni HEA and discussed its microstructure evolution and hardness changes.

Recently, a literature research of microstructure in various multicomponent alloy systems has been carefully conducted by Yang and Zhang [22], and the corresponding atomic size differences, enthalpy of mixing and entropy of mixing have been calculated. On the basis of all available data, a solid solution formation rule for multicomponent HEAs has been proposed in that paper.

It is reported in the study [24], that the high mixing entropy is not the only factor, which controls the solid solution formation in equiatomic multicomponent alloys. At the same time the formation of solid solution requires that the mixing enthalpy (ΔH_{mix}), atomic size difference (δ) and mixing entropy simultaneously satisfy some suitable ranges.

A paper concerning a nanostructured Al–Co–Cr–Cu–Fe and Ni–Co–Cr–Cu–Fe HEAs produced by mechanical alloying (MA) in metastable form and stable microstructures obtained, is given in reference [25]. It is reported in the study that the solid solution criteria proposed for HEAs need a revision to account for enthalpy of mixing between elements in a given alloy system.

A parameter quantify the atomic size difference in a multicomponent alloy has given considerable insight into the formation of Disordered Solid Solution (DSS) has been reported in [26]. It has been realized from this study that the enthalpy of mixing plays an important role and can often override the role of entropy of mixing.

THEORETICAL FUNDAMENTALS

All original traditional geometrical models were only designed for a ternary system. There are two different approaches to extend them to a higher order system: (i) extension based on all possible binary systems; (ii) extension from consideration of each possible ternary. The second one is difficult to be summarized due to many different descriptions that are hard to understand. All traditional geometric models have been generally based on the selection of a binary representative point. According to the method (i), using the weight probability,

$$W_{ij} = \frac{x_i x_j}{X_i X_j}, \quad (1)$$

the excess Gibbs free energy of a quinary system can be defined generally as follows:

$$G_{ij}^E = \frac{x_1 x_2}{X_1 X_2} G_{12} + \frac{x_1 x_3}{X_1 X_3} G_{13} + \frac{x_1 x_4}{X_1 X_4} G_{14} + \frac{x_1 x_5}{X_1 X_5} G_{15} + \frac{x_2 x_3}{X_2 X_3} G_{23} + \frac{x_2 x_4}{X_2 X_4} G_{24} + \frac{x_2 x_5}{X_2 X_5} G_{25} + \frac{x_3 x_4}{X_3 X_4} G_{34} + \frac{x_3 x_5}{X_3 X_5} G_{35} + \frac{x_4 x_5}{X_4 X_5} G_{45}. \quad (2)$$

Here, x_i and x_j represent the molar fraction of component i and j in quinary system; while X_i and X_j are the selected binary compositions which gain different values for various kinds of geometric models.

The key step in Chou's model is introducing a new concept, called as similarity coefficient ξ , into geometrical model, that is

$$\xi_{ij}^k = \left(1 + \frac{\eta_{(ji,jk)}}{\eta_{(ij,ik)}} \right)^{-1}. \quad (3)$$

Here, $\eta_{(ij, ik)}$, which is called deviation sum of squares, can be expressed as a function related to the excess Gibbs free energy of ij and ik two binaries

$$\eta_{(ij, ik)} = \int_{x_i=0}^{x_i=1} (G_{ij}^E - G_{ik}^E)^2 dX_i. \quad (4)$$

In the present study, the analytical integration procedure has been used. The obtained expressions have been found as a function of the Redlich–Kister parameters and temperature and then calculated for the alloys in mentioned above in 1373 K.

In Eq. (4), the Redlich–Kister polynomial is always used to express the excess Gibbs energy of mixing for a binary system in the following form:

$$G_{ij}^E = X_i X_j \sum_{k=0}^n \Omega_{ij}^k (X_i - X_j)^k, \quad (5)$$

X_i and X_j indicate the mole fraction of component i and j in the binary system, as a function of similarity coefficients can be calculated by:

$$X_{i(j)} = x_i + \sum_{k \neq i, j=1}^m x_k \xi_{i(j)}^k. \quad (6)$$

On the other hand, $X_{i(j)}$ can be expressed as a function of the x_i and x_j . A parameter denoted δ_{ij} , which is a parameter [13] that depends on the different models considered, i.e.,

$$X_{i(j)} = \frac{1 + x_i - x_j}{2} - \delta_{ij}. \quad (7)$$

Their expressions can be written as, in Muggianu model

$$\delta_{ij} = 0 \quad (8)$$

and in Kohler model

$$\delta_{ij} = \frac{(x_j - x_i)(1 - x_i - x_j)}{2(x_i - x_j)}. \quad (9)$$

A contribution of the ternary interactions to the excess Gibbs free energy of mixing can be written as $x_1 x_2 x_3 f$, so that f is a function of the similarity and Redlich–Kister parameters for GSM and other two models in question, respectively:

$$f = (2\xi_{12} - 1) \{ \Omega_{12}^2 [(2\xi_{12} - 1)x_3 + 2(x_1 - x_2)] + \Omega_{12}^1 \} + (2\xi_{23} - 1) \{ \Omega_{23}^2 [(2\xi_{23} - 1)x_1 + 2(x_2 - x_3)] + \Omega_{23}^1 \} + (2\xi_{31} - 1) \{ \Omega_{31}^2 [(2\xi_{31} - 1)x_2 + 2(x_3 - x_1)] + \Omega_{31}^1 \} \quad (10)$$

$$\text{and } f = x_1 x_2 x_3 P_{123}, \quad \text{where} \quad (11)$$

$$P_{123} = (x_1 \Omega_{123}^0 + x_2 \Omega_{231}^1 + x_3 \Omega_{312}^2),$$

where Ω_{123}^0 , Ω_{231}^1 , and Ω_{312}^2 can be denoted as Ω_1 , Ω_2 , and Ω_3 . In a ternary regular system, there is a relation, $\Omega_1 = \Omega_2 = \Omega_3$. Moreover, A relationship among the Ω_1 , Ω_2 , and Ω_3 can be written as $\Omega_{123} = \frac{\Omega_1 + \Omega_2 + \Omega_3}{3}$. The ternary alloys in mentioned

above, the term $x_1 x_2 x_3 (x_1 \Omega_1 + x_2 \Omega_2 + x_3 \Omega_3)$ should be added to the equations related with the ternary alloys which can be obtained from the Eq. (2).

RESULTS AND DISCUSSION

Any study considering thermodynamic calculation of mixing enthalpy from the point of view of GSM has yet been done concerning Co–Cr–Cu–Fe–Ni alloy systems in literature. The required binary interaction data have been gathered with care from the literature at the stage of mixing enthalpy calculations (Table 1). In order to calculate enthalpy of mixing alloys in question the similarity coefficients are calculated and listed in Table 2 using Eqs. (3)–(6). The article Chou et al. [13] contains the similarity coefficients associated with Ni–Cr–Co–Al–Mo system assessed at a temperature 2000 K. Some of them are: $\xi_{1(13)}^{(5)} = 0.184436$, $\xi_{1(15)}^{(3)} = 0.441363$, and $\xi_{3(35)}^{(1)} = 0.012202$. In the present study, for Co_xCrCuFeNi alloy, the values corresponding to these numbers are obtained as: $\xi_{1(13)}^{(5)} = 0.919367$, $\xi_{1(15)}^{(3)} = 0.5962213$, and $\xi_{3(35)}^{(1)} = 0.114653$. As is seen in the article of Chou et al. [13], two values (0.052704 and 0.035694) calculated from using similarity coefficients assessed at a temperature 1373 K which are obtained from the right and left sides of Chou's

Table 1. Redlich–Kister coefficients for ten fcc phase of the Co–Cu–Cr–Fe–Ni System

| System $i-j$ | Ω_{ij}^0 | Ω_{ij}^1 | Ω_{ij}^2 | References |
|--------------|----------------------|----------------------|-----------------|------------|
| (1–2)(Co–Cu) | $34600 - 4T$ | $-6410 + 3.7T$ | 4390 | [28] |
| (1–3)(Co–Cr) | $-24052.09 + 8.188T$ | $5331.825 - 6.906T$ | 0 | [29] |
| (1–4)(Co–Fe) | -8968.75 | 0 | 3528.8 | [30] |
| (1–5)(Co–Ni) | $-800 + 1.2629T$ | 0 | 0 | [31] |
| (2–3)(Cu–Cr) | $88112 - 30.38315T$ | 0 | 0 | [32] |
| (2–4)(Cu–Fe) | $48232.5 - 8.60954T$ | $8861.88 - 5.28975T$ | 0 | [32] |
| (2–5)(Cu–Ni) | $8047.72 + 3.42217T$ | $-2041.3 + 0.99714T$ | 0 | [32] |
| (3–4)(Cr–Fe) | $28871.89 - 22.318T$ | $32711.42 - 18.18T$ | 0 | [33] |
| (3–5)(Cr–Ni) | $8030 - 12.8801T$ | $33080 - 16.0362T$ | 0 | [34] |
| (4–5)(Fe–Ni) | $-15500 + 2.85T$ | $14000 - 4T$ | -3000 | [35] |

Table 2. Similarity coefficients for the Co–Cu–Cr–Fe–Ni system at 1373 K

| $\xi_{1(12)}^{(3)}$ | $\xi_{1(12)}^{(4)}$ | $\xi_{1(12)}^{(5)}$ | $\xi_{1(13)}^{(2)}$ | $\xi_{1(13)}^{(4)}$ | $\xi_{1(13)}^{(5)}$ |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 0.86682 | 0.970019 | 0.741325 | 0.340583 | 0.149114 | 0.919367 |
| $\xi_{1(14)}^{(2)}$ | $\xi_{1(14)}^{(3)}$ | $\xi_{1(14)}^{(5)}$ | $\xi_{1(15)}^{(2)}$ | $\xi_{1(15)}^{(3)}$ | $\xi_{1(15)}^{(4)}$ |
| 0.42011 | 0.287506 | 0.786229 | 0.856068 | 0.5962213 | 0.332172 |
| $\xi_{2(23)}^{(1)}$ | $\xi_{2(23)}^{(4)}$ | $\xi_{2(23)}^{(5)}$ | $\xi_{2(24)}^{(1)}$ | $\xi_{2(24)}^{(3)}$ | $\xi_{2(24)}^{(5)}$ |
| 0.07352 | 0.041196 | 0.263862 | 0.021901 | 0.063999 | 0.191995 |
| $\xi_{2(25)}^{(1)}$ | $\xi_{2(25)}^{(3)}$ | $\xi_{2(25)}^{(4)}$ | $\xi_{3(34)}^{(1)}$ | $\xi_{3(34)}^{(2)}$ | $\xi_{3(34)}^{(5)}$ |
| 0.674836 | 0.684692 | 0.472748 | 0.697208 | 0.6141 | 0.308296 |
| $\xi_{3(35)}^{(1)}$ | $\xi_{3(35)}^{(2)}$ | $\xi_{3(35)}^{(4)}$ | $\xi_{4(45)}^{(1)}$ | $\xi_{4(45)}^{(2)}$ | $\xi_{4(45)}^{(3)}$ |
| 0.114653 | 0.85832 | 0.904188 | 0.119127 | 0.790506 | 0.954901 |

Table 3. Redlich–Kister parameters associated with Ca–Sr–Yb system

| Alloys | $\Omega_{ij}^0(T)$ | $\Omega_{ij}^1(T)$ |
|-------------|--------------------|--------------------|
| Ca–Sr (1–2) | 6511 | –382 |
| Ca–Yb (1–3) | 3207 | –280 |
| Sr–Yb (2–3) | 9624 | –488 |

Ternary interactions of Ca–Sr–Yb system: $\Omega_{Ca} = 25940$ J/mol, $\Omega_{Sr} = 2913$ J/mol, $\Omega_{Yb} = -8645$ J/mol, $\Omega_{Ca-Sr-Yb} = 6736$ J/mol.

checked equation are in agreement with each other. The numerical values of the enthalpy of mixing for the quinary system mentioned above are obtained at temperatures of 1373 K and the full range of cobalt concentrations. The results are presented in Fig. 1. The

graphs reveal a decrease in the excess Gibbs free enthalpy as cobalt content increases. When a comparison among the Kohler, Muggianu and GSM models is done at the temperature 1373 K, it is seen clearly that the differences among corresponding results of enthalpy of mixing are very small. One can see from Fig. 1, which is including compositions of cobalt, which the predictions of Muggianu and Kohler models differ rather from those of GSM. It should be also noted that positive value of 3.232 kJ/mol (for Kohler and Muggianu models) and 3.0623 kJ/mol (GSM) in the solid phase have been predicted for equimolar $Co_x-Cr-Cu-Fe-Ni$ alloy where the value of x_{Co} is 0.2 (Figs. 1, 2). This result is in good agreement with that obtained from calculation based on Miedema's model [16, 18–22, 24, 26].

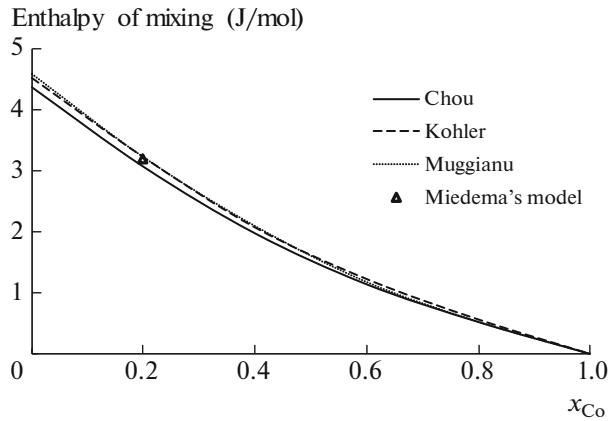


Fig. 1. A comparison of the models of GSM, Kohler and Muggianu assessed at 1373 K along the section with equimolar composition i.e., $x_{\text{Cu}} = x_{\text{Cr}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Co}})$, for the quinary alloy Co–Cu–Cr–Fe–Ni.

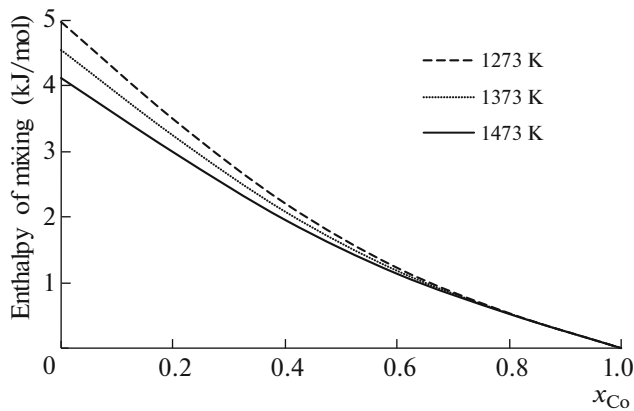


Fig. 3. In the alloy Co–Cu–Cr–Fe–Ni, the enthalpies of mixing assessed at different temperatures using Muggianu model for $x_{\text{Cu}} = x_{\text{Cr}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Co}})$.

The composition dependences of the enthalpy of mixing at 1373 K in the alloy Fe–Ni–Cr–Cu–Co, HEAs are given by using the Muggianu model. It is seen readily from Fig. 2 that, when the range of composition x are taken into consideration between 0 and 0.2, it is clear concluded that the other four elements will lead to decrease in enthalpy of mixing while the other component, Cu, will lead to increase. When the derived solutions for the enthalpy of mixing are compared, carried out in the alloy Fe–Ni–Cr–Cu–Co HEAs for the composition $x < 0.3$, i.e., the composition range of high entropy alloys. It is seen that the curves of the enthalpy of mixing performed in the present study have similar trends with those obtained from the first principle calculation's data [16].

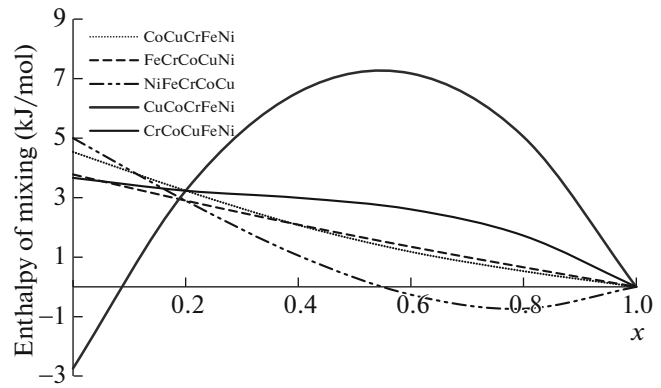


Fig. 2. A comparison of the enthalpies of mixing assessed with Muggianu model along the section with equimolar ratio for different quinary alloys at a temperature 1373 K. Here, x represents Fe, Ni, Co, Cu, and Cr contents of the alloys in question. The plots were performed for the alloys with the compositions, respectively: for the alloy Co–Cu–Cr–Fe–Ni, $x_{\text{Cu}} = x_{\text{Cr}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Co}})$; Fe–Cr–Co–Cu–Ni, $x_{\text{Cr}} = x_{\text{Co}} = x_{\text{Cu}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Fe}})$; Ni–Fe–Cr–Co–Cu, $x_{\text{Fe}} = x_{\text{Cr}} = x_{\text{Co}} = x_{\text{Cu}} = 0.25(1 - x_{\text{Ni}})$; Cu–Co–Cr–Fe–Ni, $x_{\text{Co}} = x_{\text{Cr}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Cu}})$; and Cr–Co–Cu–Fe–Ni, $x_{\text{Co}} = x_{\text{Cu}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.25(1 - x_{\text{Cr}})$.

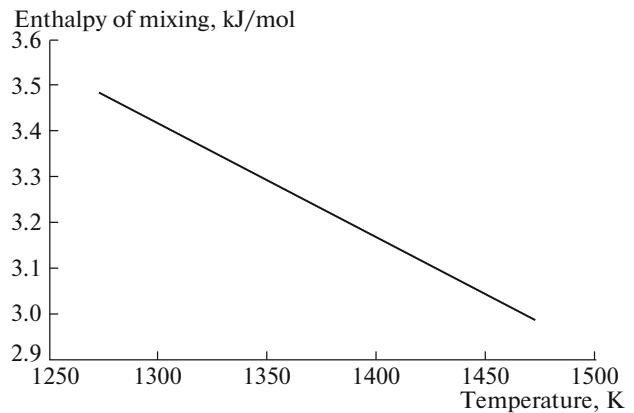


Fig. 4. The enthalpy of the equimolar quinary alloy Co–Cu–Cr–Fe–Ni with composition $x_{\text{Co}} = x_{\text{Cu}} = x_{\text{Cr}} = x_{\text{Fe}} = x_{\text{Ni}} = 0.2$ calculated with Muggianu model as a function of temperatures in the range of 1273–1473 K.

It is inferred from Figs. 3 and 4 that the enthalpy of mixing decreases as the temperature increases, when a comparison is done at small values of cobalt. When a comparison is done at the values of $x_{\text{Co}} > 0.75$, the enthalpies of mixing agree well with one another.

As far as we know, there aren't any studies in the literature that have been reported for the low-entropy ternary solid alloys, except for Ca–Sb–Yb system. In order to discuss the application of GSM and practical applicability the numerical values of the enthalpy of mixing for this system are obtained using the models just mentioned above. These models and the obtained data is compared with those for the first principle calculation's data (Fig. 5) [17]. Muggianu and Kohler

Table 4. Similarity coefficients and deviation sum of squares for GSM applied on Ca–Sr–Yb system

| Deviation sum of squares | η_1 (J ² /mol ²) = 3.63930×10^5 | | η_2 (J ² /mol ²) = 3.26630×10^5 | | η_3 (J ² /mol ²) = 13.7280×10^5 | |
|--------------------------|--|-------|--|-------|--|-------|
| Interaction of | Ca–Sr | Ca–Yb | Sr–Ca | Sr–Yb | Yb–Ca | Yb–Sr |
| | | | $\eta_3 > \eta_1 > \eta_2$ | | | |
| Similarity coeff. | $\xi_{Ca-Sr} = 0.527007$ | | $\xi_{Sr-Yb} = 0.192199$ | | $\xi_{Yb-Ca} = 0.790451$ | |

models can describe the first principle calculation's data better than those of GSM.

Recently, some thermodynamical property studies given in the introduction of this study and others dealing with the six components, quinary and quaternary alloys are continuing [36–40].

CONCLUSIONS

The results obtained in this study are as follows:

(1) A positive value of 3.2 kJ/mol of mixing enthalpy in the solid phase associated with Kohler, Muggianu, GSM models have been predicted for equimolar Co_x–Cr–Cu–Fe–Ni alloy.

(2) When the range of composition x are taken into consideration between 0 and 0.2, it is clearly concluded that the other four elements will lead to decrease in enthalpy of mixing while the other component, Cu, will lead to increase in enthalpy of mixing.

(3) Positive values of 2.7, 2.45, and 2.25 kJ/mol in the solid phase for Kohler, Muggianu, GSM models have been predicted for equimolar Ca–Sr–Yb alloy, respectively.

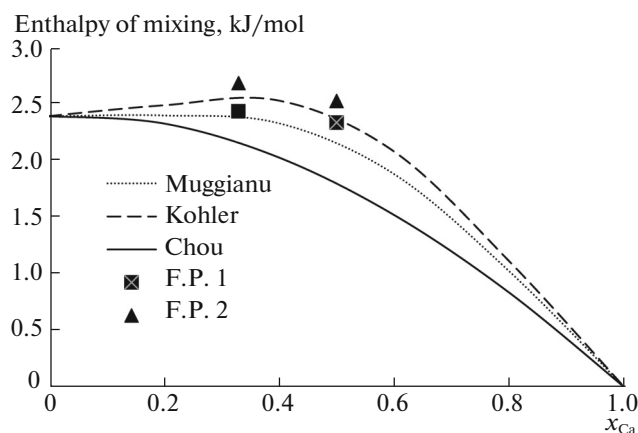


Fig. 5. A comparison of the enthalpies of mixing associated with models along the section $x_{Sr}/x_{Yb} = 1$ for the alloy Ca–Sr–Yb at a temperature 1373 K. The abbreviate F.P. 1 and F.P. 2 represent fully relaxed special quasi-random structure and fully symmetry preserved calculations, respectively.

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