Model of Decomposition of Alloy with Two Magnetic Components: the BCC FeCr System

Article *in* The Physics of Metals and Metallography · November 2021

DOI: 10.1134/S0031918X21110120

I. K. Razumov
Institute of Metal Physics

Yuri Gornostyrev
Institute of quantum materials science

ISSN 0031-918X, Physics of Metals and Metallography, 2021, Vol. 122, No. 11, pp. 1031–1038. © Pleiades Publishing, Ltd., 2021.
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Model of Decomposition of Alloy with Two Magnetic Components: the BCC FeCr System

I. K. Razumov[a, *] **and Yu. N. Gornostyrev**[a, b]

[a] Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Ekaterinburg, 620108 Russia
[b] Ural Federal University Named after Boris Yel'tsin, Ekaterinburg, 620002 Russia
*e-mail: rik@imp.uran.ru

Received July 6, 2021; revised July 22, 2021; accepted July 23, 2021

Abstract—A sequential model of the decomposition of the bcc FeCr binary alloy is formulated that takes into account the configurational and magnetic contributions to the free energy. Using the results of ab initio calculations, the theory of regular solutions is generalized by considering the contributions of the magnetic entropy, the concentration dependence of the exchange interactions, and the mixing energies. The resulting expression for the free energy makes it possible to construct the boundaries of the two-phase region of the bcc FeCr alloy in good agreement with the experimental data, as well as to predict the position of the spinodal, below which the formation of highly dispersed states should be expected when starting from a homogeneous state.

Keywords: spinodal decomposition, magnetism, first principle parametrization, Oguchi approach, Hellmann–Feynman theorem

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1. INTRODUCTION

The Fe–Cr binary alloy is the basis of many important industrial steels, especially those used in the nuclear power industry, in which high resistance to radiation and corrosion is required [1, 2]. It was established that the Fe–Cr alloy with a low Cr content (less than 12 at %) exhibits anomalous phase stability in the ferromagnetic state [3–6]. On the other hand, there is a wide region of immiscibility in the Fe–Cr system, within which the alloy decomposes into phases with high and low chromium contents [3, 7] that can cause embrittlement of steel [8].

To preserve and improve the performance characteristics of the alloy, alloying element additives are used, such as Ni, Mn, Mo, Co, etc. Thus, the three-component Fe–Cr–Co alloy demonstrates high corrosion resistance, plasticity, and the thermal stability of magnetic properties. In this case, high magnetic properties of this alloy are achieved in a highly dispersed state that is formed as a result of spinodal decomposition of a homogeneous state into the α_1 ferromagnetic phase depleted in Cr and the α_2 paramagnetic phase enriched in Cr [9].

To select the optimal composition and heat treatment conditions that provide the required properties of alloys, a deep understanding of physical mechanisms that determine the formation and stability of their structural state is required. The enthalpy of mixing of the Fe–Cr alloy in the para- and ferromagnetic states was calculated within the density functional theory (DFT) in [4, 10, 11]. It was shown that the mixing energy of the Fe–Cr binary alloy depends significantly on the chromium concentration. According to the results of ab initio calculations, the enthalpy of mixing increases by a factor of approximately 1.5 (at a chromium concentration of 50 wt %) upon the transition from the paramagnetic to ferromagnetic state and, on the contrary, it decreases and becomes negative at a chromium concentration of less than 10 wt % [4, 10]. As shown in [12], the anomalous behavior of the enthalpy of mixing can be explained within the framework of a model that takes into account the temperature dependence of the magnetic contribution.

Thus, the theory of decomposition in the Fe–Cr system should take into account the magnetic and lattice degrees of freedom, as well as their influence on each other. As a result, the effective potentials of interatomic interactions—and, consequently, the mixing energy and the Curie temperature—should depend on the concentration of the components. In addition, the short-range magnetic order at temperatures above the Curie temperature (see discussion in [13]) and the contribution of the magnetic entropy—that is not negligible [14]—should be taken into account.

To date, there is no consistent theory that takes into account the listed features of the alloy. The mutual influence of the magnetic and chemical orderings in binary alloys within the phenomenological approach has been actively discussed in a number of studies (see, for example, the review article [15]). The proposed approaches made it possible to consider the qualitative features of the interaction between the magnetic and chemical subsystems, but turned out to be insufficient for a quantitative description of the thermodynamics of the alloys under consideration.

Recently, theoretical concepts of the decomposition of alloys that contain magnetic components have been further developed [13, 16–19] owing to the emergence of new experimental data and ab initio calculation results. The role of magnetism in the decomposition of Fe–Cr alloys was discussed in [16]. In [17, 18], the use of the method of magnetic cluster decomposition made it possible to propose a consistent approach to the description of the thermodynamics and kinetics of the decomposition of Fe–Cr alloys. In [19], attention was drawn to the fact that the use of the ab initio mixing energies leads to significant overestimation of the decomposition temperature. To solve this problem, the authors of [19] proposed to use the temperature-dependent mixing energy, which made it possible to obtain a solubility curve in agreement with the experiment. In [13], the transition to concentration-dependent interactions was used to describe the decomposition in a binary alloy with one magnetic component (bcc FeCu).

It should be noted that the boundary of the two-phase region of the bcc FeCr alloy at elevated temperatures is successfully calculated [20] by the methods of theoretical thermodynamics implemented in the CALPHAD software package; however, the question of the nonzero solubility of chromium in the limit at $T = 0$ K [21], in which the data are extremely contradictory, still remains arguable.

In this study, we formulate a model for the decomposition of an alloy with two magnetic components that eliminates the disadvantages of the previous approaches and takes into account the magnetic contributions to the enthalpy and entropy of the system. The model is parameterized using the ab initio calculation results. We show that it is of crucial importance to take into account the concentration dependences of the effective interactions and exchange parameters for a correct description of phase equilibria in the Fe–Cr system.

2. FREE MIXING ENERGY OF AN ALLOY WITH TWO MAGNETIC COMPONENTS

The alloy mixing enthalpy has the following form

$$H_{\text{mix}}(T,\{c_\alpha\}) = H(T,\{c_\alpha\}) - E_\alpha^{\text{pure}}(T)c_\alpha, \qquad (1)$$

where $H(T,\{c_\alpha\})$ is the enthalpy of the alloy; $E_\alpha^{\text{pure}}(T)$ and c_α are the energy of pure component α and its atomic concentration ($\alpha = \{\text{Fe, Cr}\}$), respectively. Hereinafter, we assume for brevity that summation is performed over repeated indices in the products.

We can represent $H_{\text{mix}}(T, \{c_\alpha\})$ as a sum of the paramagnetic (PM) and magnetic contributions, as follows:

$$H_{\text{mix}}(T,\{c_\alpha\}) = H_{\text{mix}}^{\text{PM}}(\{c_\alpha\}) + H_{\text{mix}}^{\text{magn}}(T,\{c_\alpha\}), \qquad (2)$$

We take the mixing enthalpy in the PM state in accordance with the standard model of a regular solid solution [22], as follows:

$$H_{\text{mix}}^{\text{PM}} = -v_{\text{FeCr}}^{\text{PM}} c_{\text{Cr}} c_{\text{Fe}}, \qquad (3)$$

where $v_{\text{FeCr}}^{\text{PM}}$ is the mixing energy of the components in the PM state.

We write the magnetic contribution to the enthalpy of mixing in the Heisenberg form, as follows:

$$H_{\text{mix}}^{\text{magn}} = J_{\alpha\alpha}^0 Q_{\alpha\alpha}^0 c_\alpha - J_{\alpha\alpha} Q_{\alpha\alpha} c_\alpha^2 - 2J_{\text{FeCr}} Q_{\text{FeCr}} c_{\text{Fe}} c_{\text{Cr}}, \qquad (4)$$

where J_{FeCr} is the energy of magnetic exchange between the Fe and Cr atoms that depends on local concentrations of the components; $Q_{\alpha\beta} = \langle \mathbf{m}_\alpha \mathbf{m}_\beta \rangle / (|m_\alpha||m_\beta|)$ is the correlator of the magnetic moments of the nearest neighbors of α and β atoms; $J_{\alpha\alpha}^0 = J_{\alpha\alpha}(c_\alpha = 1)$, and $Q_{\alpha\alpha}^0 = Q_{\alpha\alpha}(T, c_\alpha = 1)$. It should be noted that the correlator value varies, by virtue of the definition, within the range of $-1 < Q_{\alpha\beta} < 1$, and the absolute values of the magnetic moments are included in the definition of exchange energies $J_{\alpha\beta}$. It is possible to generalize the mean field method [23] used here by the cluster expansion [24]; its generalization to the case of an alloy with magnetic components, i.e., magnetic cluster expansion (MCE), was considered in [25, 26]. Here, we restrict ourselves to the mean-field approximation, but we will assume that the effective interactions in the alloy depend on the local concentration.

The calibration contributions linear with respect to concentrations in formula (4) affect neither the thermodynamics nor the kinetics of transformations, but ensure that the formulas agree with the definition of the term “mixing enthalpy” according to Eq. (1). They correspond to the magnetic energies of the pure components taken in appropriate proportions. It should be noted that the nonmagnetic parts of the energies of the pure components are included in the definition of $H_{\text{mix}}^{\text{PM}}$ according to Eq. (3).

Further, we simplify Eqs. (2)–(4) by substitution in the form of $c_{\text{Fe}}^2 = c_{\text{Fe}}(1 - c_{\text{Cr}})$. As a result, we have

$$H_{\text{mix}} = -v_{\text{FeCr}} c_{\text{Cr}} c_{\text{Fe}} + J_{\alpha\alpha}^0 Q_{\alpha\alpha}^0 c_\alpha - J_{\alpha\alpha} Q_{\alpha\alpha} c_\alpha, \qquad (5)$$

where

$$v_{\text{FeCr}}(T) = v_{\text{FeCr}}^{\text{PM}} + J_{\text{FeCr}}^{\text{mix}}(T), \qquad (6)$$

$$J_{\text{FeCr}}^{\text{mix}} = 2J_{\text{FeCr}} Q_{\text{FeCr}} - J_{\text{FeFe}} Q_{\text{FeFe}} - J_{\text{CrCr}} Q_{\text{CrCr}}. \qquad (7)$$

We calculate the spin correlators using the Oguchi model that is used to describe the short-range magnetic order in ferro- and antiferromagnets that are comprised of atoms of the same type [14, 27]. This approach uses the approximation of paired clusters, in which the interaction of each spin with one of the neighbors is taken into account precisely and the interaction with the remaining $z - 1$ spins is replaced by the effective Weiss field (z is the coordination number). Here, we generalize the Oguchi model to the case of an alloy and assume that the spin correlator is related to the Weiss field acting on the selected pair of spins, as follows:

$$Q_{\alpha\alpha} = \frac{\left(2\cosh\left[h_{\mathrm{W}}^{(\alpha)}\right] + 1\right) - 3\exp\left[-2j_{\alpha\alpha}\right]}{\left(2\cosh\left[h_{\mathrm{W}}^{(\alpha)}\right] + 1\right) + \exp\left[-2j_{\alpha\alpha}\right]}; \tag{8}$$

$$h_W^{(\alpha)} = H_{\mathrm{W}}^{(\alpha)}/kT, \quad j_{\alpha\alpha} = J_{\alpha\alpha}/(zkT), \tag{9}$$

where $H_{\mathrm{W}}^{(\alpha)}$ is the Weiss field around an α atom. In this study, we restrict ourselves to analyzing the states of the FeCr alloy at temperatures substantially higher than the Néel temperature of chromium ($T_{\mathrm{N}} = 311$ K) and assume that the short-range antiferromagnetic order in this case is absent or negligible at any concentration. Therefore, the effective Weiss fields around atoms of each type can be determined without accounting for the difference in magnetic sublattices, as follows:

$$\frac{z}{z-1} H_{\mathrm{W}}^{(\alpha)} = J_{\alpha\beta} c_{\beta} \sigma_{\beta}, \tag{10}$$

where σ_α the mean value of the reduced magnetic moment ($0 < \sigma_\alpha < 1$) of an α atom that corresponds to the given local concentrations of the components and depends on the temperature. Formula (10) neglects the corresponding pair correlations, so that the σ_α values can be considered independent of the type of the atom around which they are calculated. The σ_α values are determined from the following system of transcendental equations:

$$\sigma_\alpha(T) = \frac{2\sinh\left[h_{\mathrm{W}}^{(\alpha)}\right]}{\exp\left[-2j_{\alpha\alpha}\right] + 1 + 2\cosh\left[h_{\mathrm{W}}^{(\alpha)}\right]}. \tag{11}$$

Using formulas (8)–(11), it is possible to find $Q_{\alpha\alpha}$, but the values of the correlators of different types of spins remain undefined. It should be noted that if we neglect the difference between the short-range and long-range magnetic orders (which is an adequate approximation below the Curie temperature), then $Q_{\alpha\beta}$ and σ_α are related in an obvious way, as follows:

$$Q_{\alpha\alpha} = \sigma_\alpha^2, \quad Q_{\alpha\beta} = \sigma_\alpha \sigma_\beta. \tag{12}$$

In this case,

$$Q_{\alpha\beta} = \operatorname{sgn}(\sigma_\alpha)\operatorname{sgn}(\sigma_\beta)\sqrt{\left|Q_{\alpha\alpha} Q_{\beta\beta}\right|}. \tag{13}$$

It is reasonable to assume that formula (13) is an adequate approximation for $Q_{\alpha\beta}$ even if the $Q_{\alpha\alpha}$ values are calculated with accounting for the short-range magnetic order above the Curie temperature.

It follows from formulas (6)–(13) that magnetism leads, first of all, to a change in the mixing energy $v_{\alpha\beta}$, within the considered model; moreover, the latter turns out to be dependent on the temperature and the concentrations of the components due to the adopted form of correlators (8) and (12) with Weiss fields (10).

Next, we determine the free mixing energy that includes, in addition to mixing enthalpy (5), the contributions of configurational entropy $S_{\mathrm{mix}}^{\mathrm{conf}}$ and magnetic entropy $S_{\mathrm{mix}}^{\mathrm{magn}}$:

$$G_{\mathrm{mix}}\left(T, \{c_\alpha\}\right) = G_{\mathrm{mix}}^{\mathrm{PM}} + G_{\mathrm{mix}}^{\mathrm{magn}}; \tag{14}$$

$$G_{\mathrm{mix}}^{\mathrm{PM}} = H_{\mathrm{mix}}^{\mathrm{PM}} - TS_{\mathrm{mix}}^{\mathrm{conf}}; \tag{15}$$

$$G_{\mathrm{mix}}^{\mathrm{magn}} = H_{\mathrm{mix}}^{\mathrm{magn}} - TS_{\mathrm{mix}}^{\mathrm{magn}}. \tag{16}$$

We define the configurational entropy within the model of a regular solid solution in the following way:

$$S_{\mathrm{mix}}^{\mathrm{conf}} = -kc_\alpha \ln c_\alpha. \tag{17}$$

To take into account the contribution of the magnetic entropy, we use the early published approach [14, 28], in which the free energy is calculated from the enthalpy using the Hellmann–Feynman theorem. As a result, we have:

$$G_{\mathrm{mix}}^{\mathrm{magn}} = c_\alpha \int_0^{J_{\alpha\alpha}^0} Q_{\alpha\alpha}^0 dJ_{\alpha\alpha} - c_\alpha \int_0^{J_{\alpha\alpha}} Q_{\alpha\alpha} dJ_{\alpha\alpha} - c_{\mathrm{Cr}} c_{\mathrm{Fe}} I_{\mathrm{FeCr}}^{\mathrm{mix}}, \tag{18}$$

$$I_{\alpha\beta}^{\mathrm{mix}} = 2\int_0^{J_{\alpha\beta}} Q_{\alpha\beta} dJ_{\alpha\beta} - \int_0^{J_{\alpha\alpha}} Q_{\alpha\alpha} dJ_{\alpha\alpha} - \int_0^{J_{\beta\beta}} Q_{\beta\beta} dJ_{\beta\beta}. \tag{19}$$

At the temperatures substantially higher than the Curie temperature, at which the correlation of neighboring spins is negligible, we find from Eq. (18) that $G_{\mathrm{mix}}^{\mathrm{magn}} \approx 0$, and expression (14) is reduced to the free mixing energy of a binary alloy in the standard model of a regular solid solution [22].

3. PARAMETRIZATION OF THE MODEL

3.1. Approximation of Concentration-Independent Parameters

For pure component α, the exchange energy is related to the Curie temperature by relation $kT_{\mathrm{C}}^{(\alpha)}(c_\alpha = 1) = qJ_{\alpha\alpha}$ [29]. According to the ab initio calculation results, the exchange energy in pure iron is $J_{\mathrm{FeFe}} = 0.18$ eV/at. [30]. Hence, we obtain a correction factor value of $q \approx 0.5$ when taking into account an

Table 1. Model parameters (eV/at.) obtained by fitting the mixing enthalpy to the ab initio calculation results [10]

c_{Cr}	$H_{\mathrm{mix}}^{\mathrm{PM}}$	$v_{\mathrm{FeCr}}^{\mathrm{PM}}$	$H_{\mathrm{mix}}^{\mathrm{FM}}$	$v_{\mathrm{FeCr}}^{\mathrm{FM}}$	$J_{\mathrm{FeCr}}^{\mathrm{mix(FM)}} = v_{\mathrm{FeCr}}^{\mathrm{FM}} - v_{\mathrm{FeCr}}^{\mathrm{PM}}$	$J_{\mathrm{FeCr}} = -\left(J_{\mathrm{FeCr}}^{\mathrm{mix(FM)}} + J_{\mathrm{FeFe}} + J_{\mathrm{CrCr}}\right)/2$
0.5	0.070	–0.28	0.095	–0.38	–0.10	–0.01

experimentally known Curie temperature value of $T_{\mathrm{C}}^{(\mathrm{Fe})} = 1043$ K.

Following [11] and assuming that similar relation $kT_{\mathrm{N}} = -qJ_{\mathrm{CrCr}}$ is valid for the Néel temperature of chromium, we determine the J_{CrCr} value. Hence, we have $J_{\mathrm{CrCr}} = -0.054$ eV/at. when taking into account that the experimental value the Néel temperature is $T_{\mathrm{N}} = 311$ K.

Remaining unknowns $\nu_{\mathrm{FeCr}}^{\mathrm{PM}}$ and J_{FeCr} can be determined using the ab initio calculation results for the mixing enthalpy [10] in paramagnetic ($Q_{\alpha\beta} = 0$) and ferromagnetic states, and equations (6) and (7). First, we find $\nu_{\mathrm{FeCr}}^{\mathrm{PM}}$ assuming that the concentrations of the Fe and Cr components are 0.5 and $Q_{\alpha\beta} = 0$ in the paramagnetic state. Next, we take into account the $J_{\alpha\alpha}$ values defined above for the ferromagnetic state and find J_{FeCr}. For this, the values of the corresponding correlators at $T = 0$ K should be taken as $Q_{\alpha\beta}$ in formula (7). In this case, $Q_{\mathrm{FeFe}} = 1$. It is well known that the Q_{CrCr} correlator at $T = 0$ K alternates its sign at a certain chromium concentration [16]. At a low chromium concentration, the chromium spins are oriented oppositely to the iron spins ($Q_{\mathrm{FeCr}} = -1$) and, consequently, become codirectional with respect to each other, so that $Q_{\mathrm{CrCr}} = 1$. The obtained results of the assessment are given in Table 1. It should be noted that the alloy becomes antiferromagnetic at a high chromium concentration and $Q_{\mathrm{CrCr}} = -1$, which is not taken into account in this approximation.

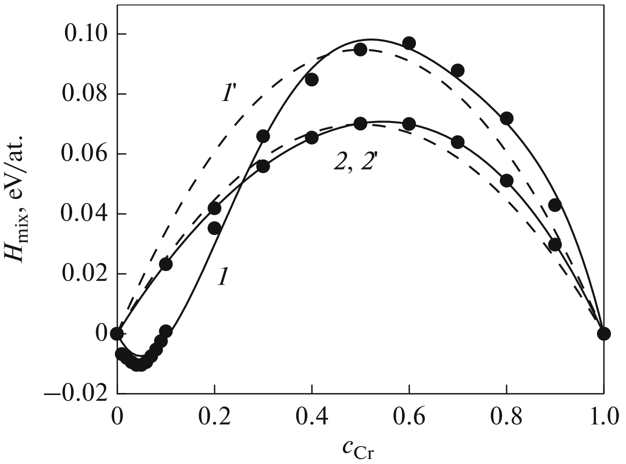

Fig. 1. Mixing enthalpy of the FeCr binary alloy in the ferromagnetic (*1*) and paramagnetic (*2*) states as a function of the chromium concentration. The circles denote the ab initio calculation results [10], the solid lines correspond to the approximation of the calculated data by polynomials (22), and dashed lines *1*' and *2*' are plotted in the approximation of concentration-independent parameters (see Table 1).

It follows from the results of comparison with experimental data that the $\nu_{\mathrm{FeCr}}^{\mathrm{PM}}$ value is overestimated (in absolute value), which may be due to the unaccounted contribution of the vibrational entropy to the free energy of the alloy. According to [11, 31], the mixing energy of the Fe–Cr alloy is described by the following empirical formula:

$$v_{\mathrm{FeCr}}^{(\mathrm{exp})} = -0.26(1 - 0.000467T)\ (\mathrm{eV/at.}). \qquad (20)$$

Hence, $v_{\mathrm{FeCr}}^{\mathrm{FM(exp)}} = -0.26$ eV/at. in the ferromagnetic state ($T = 0$ K) and $v_{\mathrm{FeCr}}^{\mathrm{PM(exp)}} = -0.11$ eV/at. in the paramagnetic state ($T \approx 1200$ K).

It should be noted that the position of the dome of the two-phase region in the model of a regular solid solution [22] is determined by the following relation:

$$kT_{\mathrm{binod}} = v_{\mathrm{FeCr}}^{\mathrm{PM}}(1 - c_{\mathrm{Cr}})/\ln\left[c_{\mathrm{Cr}}/(1 - c_{\mathrm{Cr}})\right], \qquad (21)$$

so we obtain $T_{\mathrm{binod}} \approx 650$ K when choosing $v_{\mathrm{FeCr}}^{\mathrm{PM}} = -0.11$ eV/at., while the top of the dome of two-phase region $\alpha_1 + \alpha_2$ in the phase diagram of the Fe–Cr alloy in the absence of an ordered σ phase [7, 32] is located at $T_{\mathrm{binod}} \approx 800$ K. It is logical to assume that an increase in the decomposition temperature by 150 to 200 degrees compared to the estimate based on the $v_{\mathrm{FeCr}}^{\mathrm{PM}}$ value is caused by the presence of the magnetic ordering that is substantial at this temperature. Further, we use empirical value $v_{\mathrm{FeCr}}^{\mathrm{PM}} = -0.11$ eV/at., while the rest of the parameters are taken from Table 1. The mixing enthalpy of the FeCr alloy in the approximation of concentration-independent parameters is shown by dashed lines in Fig. 1. As can be seen from Fig. 1, this approximation describes well the paramagnetic state, but does not reproduce the features of the behavior of H_{mix} at low chromium concentrations in the ferromagnetic state.

3.2. Concentration Dependences of the Mixing and Magnetic Exchange Energies

The approximation of concentration-independent energy parameters does not allow one to take into account the change in the sign of the mixing energy at low temperatures in the range of chromium concentrations below 10%, due to which the diluted Fe–Cr alloy should remain stable at low temperatures [4, 10, 11].

In [10], the mixing enthalpy of the Fe–Co–Cr system was calculated by the EMTO–CPA method in the paramagnetic and ferromagnetic states for arbitrary concentrations of the components. These data are insufficient for the parametrization of the discussed model because all $J_{\alpha\beta}$ values must be known for determining the $H_{\rm mix}$ values at intermediate temperatures (see formula (7)). In [33], the $J_{\rm FeFe}$, $J_{\rm CrCr}$, and $J_{\rm FeCr}$ exchange energy values were calculated at a chromium concentration of less than 30 at %, but their behavior at high concentrations is unknown. We restrict ourselves to the approximation, in which $J_{\alpha\alpha}$ does not depend on the concentration of the components. This simplification is supported by the fact that the dependence of $J_{\rm FeCr}$ on the chromium concentration is more pronounced in comparison with $J_{\rm CrCr}$, and especially in comparison with $J_{\rm FeFe}$ [33]. The parameterization proposed below should be understood as a transition to effective exchange energy $J_{\rm FeCr}$ that contains the unaccounted concentration dependence of the exchange energies.

The ab initio calculation results [10] for the mixing enthalpy of the Fe–Cr alloy in the ferromagnetic and paramagnetic states are approximated by the following polynomials of type $A_{ni}^{\rm FM(PM)} c_\alpha^{n-1}$ (see Fig. 1), where n takes values in the range from 1 to 4:

$$H_{\rm mix}^{\rm FM(PM)} = A_n^{\rm FM(PM)} c_{\rm Cr}^{n-1} c_{\rm Cr} \left(1 - c_{\rm Cr}\right). \tag{22}$$

The $A_n^{\rm FM(PM)}$ coefficients (eV/at.) are as follows:

$$A^{\rm FM} = \left(-0.33,\ 3.68,\ -6.28,\ 3.60\right), \tag{23}$$

$$A^{\rm PM} = \left(0.26,\ -0.03,\ 0.15,\ -0.03\right). \tag{24}$$

From equation (22), we have

$$v_{\rm FeCr}^{\rm PM} = B_n c_{\rm Cr}^{n-1}, \tag{25}$$

where $B_n = -A_n^{\rm PM}$. To bring into agreement with empirical data, we take $B_1 = -0.0917$ eV/at., which corresponds to the introduction of a correction (the same value as in Section 3.1) into the zero contribution of the chromium concentration to the $v_{\rm FeCr}^{\rm PM}$ energy.

The magnetic contribution to the mixing energy in the ferromagnetic state is

$$J_{\rm FeCr}^{\rm mix(FM)} = \left(A_{n1}^{\rm PM} - A_{n1}^{\rm FM}\right) c_{\rm Cr}^{n-1}. \tag{26}$$

Finally, the exchange energy of unlike atoms is calculated using formula (7) at $T = 0$ K. Since the proposed model does not take into account the antiferromagnetic phase transition at $T_{\rm N} = 311$ K, it is preferable, just like in the previous section, to choose $Q_{\rm FeFe} = 1$, $Q_{\rm CrCr} = 1$, and $Q_{\rm FeCr} = -1$ when calculating $J_{\rm FeCr}$, which enables the most adequate description of the behavior of $J_{\rm FeCr}$ at low chromium concentrations. As a result, we have

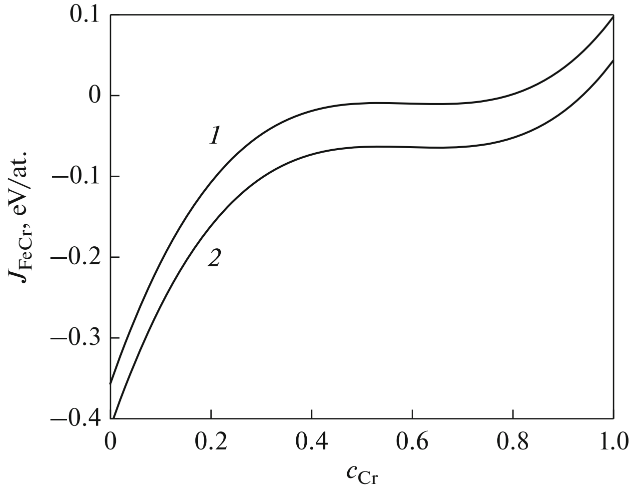

Fig. 2. Exchange energy $J_{\rm FeCr}(c_{\rm Cr})$ from the data of ab initio calculations [10] and formula (27) when choosing $Q_{\rm CrCr} = 1$ (curve *1*) and $Q_{\rm CrCr} = -1$ (curve *2*).

$$J_{\rm FeCr} = -\left(J_{\rm FeCr}^{\rm mix(FM)} + J_{\rm FeFe} + J_{\rm CrCr}\right)\Big/2. \tag{27}$$

Figure 2 shows the results of calculating the $J_{\rm FeCr}$ values when choosing $Q_{\rm CrCr} = 1$ (curve *1*) and $Q_{\rm CrCr} = -1$ (curve *2*). As can be seen from Fig. 2, the concentration dependence turns out to be very strong, so that it cannot be neglected when analyzing the role of magnetism in the decomposition. In this case, the choice of the $Q_{\rm CrCr}$ value has an insignificant effect on the value and qualitative behavior of $J_{\rm FeCr}$.

3.3. Temperature Dependences of $Q_{\alpha\alpha}$

Figure 3 shows the temperature dependences of correlators $Q_{\alpha\alpha}$ and the corresponding mean values of reduced magnetic moments σ_α that are constructed using formulas (8) and (11) with accounting for the concentration dependence of $J_{\rm FeCr}$ (Fig. 2) in different alloy compositions. The fact that the subsystems of two types of atoms have identical Curie temperature $T_{\rm C}$ (at which $\sigma_\alpha = 0$ is attained) is a common feature. The $Q_{\alpha\alpha}$ correlators have a break point at $T = T_{\rm C}$ and remain nonzero at $T > T_{\rm C}$, i.e., at the temperatures corresponding to the conservation of only short-range magnetic order. The $Q_{\rm CrCr}$ correlator takes positive values at low temperatures and low chromium concentrations (Fig. 3a, curve *2*) and negative values in other cases. Moreover, the reduced magnetic moments of chromium ($\sigma_{\rm Cr}$) and iron ($\sigma_{\rm Fe}$) are directed oppositely in any case (compare curves *1*' and *2*' in Fig. 3).

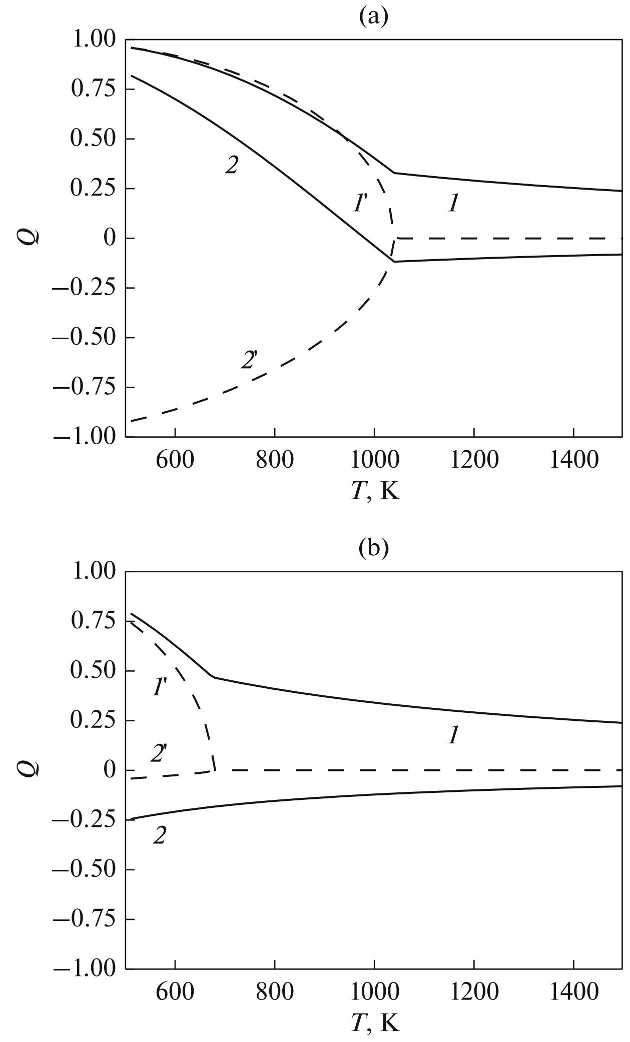

Fig. 3. Temperature dependences of the Q_{FeFe} (*1*) and Q_{CrCr} (*2*) correlators and the corresponding mean values of reduced magnetic moments σ_{Fe} (*1'*) and σ_{Cr} (*2'*) at (a) $c_{\text{Cr}} = 0.1$ and (b) $c_{\text{Cr}} = 0.4$.

4. PHASE DIAGRAM OF THE Fe–Cr ALLOY

The boundaries of the phase instability region are determined from the following system of equations that describe the equality of the chemical potentials of the components in the resulting phases (phase equilibrium condition) [22]:

$$\left.\frac{\partial G_{\text{mix}}}{\partial c_\alpha}\right|_{(1)} = \left.\frac{\partial G_{\text{mix}}}{\partial c_\alpha}\right|_{(2)} = \frac{G_{\text{mix}}^{(2)} - G_{\text{mix}}^{(1)}}{c_\alpha^{\text{eqv}(2)} - c_\alpha^{\text{eqv}(1)}}. \qquad (28)$$

Figure 4 shows the results of calculating the solubility curve of the binary Fe–Cr alloy in various approximations considered above (curves *1*–*4*) compared to the experimental data (curve *5*). For a correct comparison with experiment, the ordered σ phase and associated two-phase regions $\alpha_1 + \sigma$ and $\alpha_2 + \sigma$ are excluded from consideration in the diagram when analyzing the decomposition of the solid solution by reaction $\alpha \to \alpha_1 + \alpha_2$.

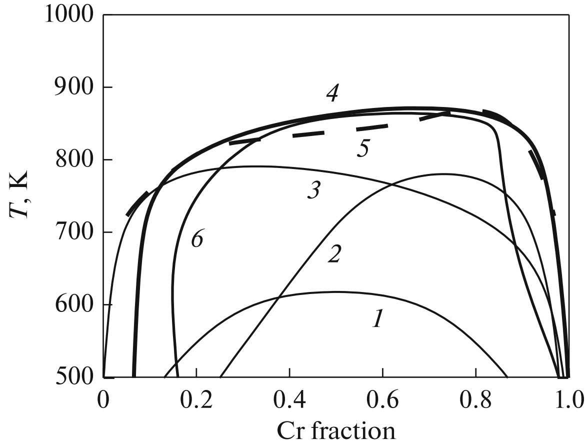

Fig. 4. Solubility curve of the binary Fe–Cr alloy for the following cases: (*1*) in the absence of a magnetic contribution to the free energy with a concentration-independent mixing energy ($v_{\text{FeCr}} = -0.11$ eV/at.); (*2*) in the absence of a magnetic contribution to the free energy with a concentration-dependent mixing energy; (*3*) in the approximation of concentration-independent energy parameters; (*4*) taking into account the dependence of the energy parameters on the concentrations of the components; (*5*) the experimental solubility curve according to the published data [34]; (*6*) the calculated spinodal curve taking into account the concentration dependence of the parameters.

The best agreement with the experiment is achieved when the concentration dependence of the parameters is taken into account (curve *4*). Herewith, the model predicts an anomalously high solubility of chromium (~8 at % at $T = 500$ K). The latter fact has no reliable experimental confirmation [21], since the known experimental data refer to higher temperatures (curve *5*) and become extremely contradictory at low temperatures.

To understand the morphological features of the precipitates settled during the decomposition of the alloy, it is also useful to consider the spinodal (Fig. 4, curve *6*) that limits the region of absolute instability of the homogeneous state from above. According to the definition given in [22], the free energy of the alloy inside the spinodal region is a convex function of concentration, i.e.,

$$\frac{\partial^2 G_{\text{mix}}(c_{\text{Cr}})}{\partial c_{\text{Cr}}^2} < 0, \qquad (29)$$

so that the alloy turns out to be unstable with respect to composition fluctuations. Between the spinodal and the solubility curve, decomposition can occur after the incubation period, according to the mechanism of nucleation and growth of precipitates. Even if the transition from the regime of absolute instability to the regime of nucleation and growth of precipitates with varying temperature or composition in a real alloy is accomplished smoothly, i.e., without a physically distinguished line [35], the spinodal is a clear qualitative reference point that allows one to estimate the tendency of a homogeneous alloy to decompose. The spinodal constructed within the developed model (Fig. 4, curve *6*) turns out to be quite close to the spinodal found experimentally [36].

5. DISCUSSION

A sequential model is proposed for describing the decomposition of an alloy with two magnetic components that generalizes the theory of regular solutions by taking into account the concentration dependences of the mixing energies and exchange interaction parameters. In contrast to the previously proposed approaches (see discussion in [15]), we take into account the difference in the behavior of the correlation functions of the magnetic moments of atoms of different types. The latter is especially important for the FeCr alloy with different signs of the Q_{FeFe} and Q_{FeCr} correlation functions, which makes it inadmissible to use approximations of type $Q_{\alpha\beta} = Q$. In addition, the model takes into account the short-range magnetic ordering above the Curie temperature, which is necessary for a correct description of the solubility limit in alloys with magnetic components [13].

To determine the contribution of the magnetic entropy to the free energy of the alloy, we used the Hellmann–Feynman theorem [28]. In the proposed model, this contribution is insignificant at low impurity concentrations (<5 at %), but becomes important when analyzing the stability conditions for a homogeneous alloy at high concentrations.

The model was parameterized using the published ab initio calculation results [10, 11, 33]. However, the use of the calculated value of mixing energy $v_{\mathrm{FeCr}}^{\mathrm{PM}}$ would lead to an overestimation of the onset temperature of decomposition by about a factor of two; a similar conclusion was also made in [19]. It can be assumed that this is caused by the unaccounted contribution of the vibrational entropy to the free energy of the alloy, the role of which in the Fe–Cr system can be large [37]. Within the developed model, the contribution of the vibrational entropy was determined by the transition to the effective $v_{\mathrm{FeCr}}^{\mathrm{PM}}$ parameter value agreed with the experimental data.

The obtained boundaries of solubility and spinodal decomposition in the Fe–Cr system (Fig. 4) are in good agreement with the known experimental data [34, 36]. Furthermore, a correct accounting for the magnetic contributions to the free energy, as well as the concentration dependence of the model parameters, was needed for a correct description of the behavior of the system under consideration. It should be noted that the latter circumstance is especially important for alloys with magnetic components, since the interaction energy between Cr atoms depends on the magnetic state that varies, in turn, with a change in the concentration of the alloying element.

Though a conclusion follows from the ab initio calculation results and the results given in Fig. 4 that the Fe–Cr alloy is anomalously stable at a low chromium content [4–6], the currently available experimental data do not reveal such a tendency [21]. Most of the experiments were carried out at $T > 500$ K, and the use of these data for low temperatures should be considered an extrapolation [21]. Therefore, the question of the solubility of chromium in iron in the low temperature limit remains controversial and requires further investigations.

6. CONCLUSIONS

To describe the decomposition processes in the bcc FeCr system on the basis of the ab initio calculation results, a sequential model that takes into account the configurational and magnetic contributions to the free energy of the alloy has been formulated. The calculated boundaries of solubility and spinodal instability of the Fe–Cr system are in good agreement with the known experimental data. It is shown that the anomalous behaviors of the mixing energy and the solubility limit of chromium at low temperatures are associated with the concentration dependence of the Fe–Cr exchange interaction energy.

FUNDING

This study was performed within the framework of State Assignment from the Ministry of Education and Science of Russia (topic Structure, no. AAAA-A18-118020190116-6).

REFERENCES

1. S. I. Porollo, A. M. Dvoriashin, A. N. Vorobyev, and Yu. V. Konobeev, “The microstructure and tensile properties of Fe–Cr alloys after neutron irradiation at 400°C to 5.5–7.1 dpa,” J. Nucl. Mater. **256**, 247–253 (1998).
2. F. Garner, M. B. Toloczko, and B. H. Sencer, “Comparison of swelling and irradiation creep behavior of fcc-austenitic and bcc-ferritic/martensitic alloys at high neutron exposure,” J. Nucl. Mater. **276**, 123–142 (2000).
3. R. O. Williams and H. W. Paxton, “The nature of aging of binary iron–chromium alloys around 500°C,” J. Iron Steel Institute, 358–374 (1957).
4. P. Olsson, I. A. Abrikosov, and J. Wallenius, “Electronic origin of the anomalous stability of Fe-rich bcc Fe–Cr alloys,” Phys. Rev. B **73**, 104416 (2006).
5. T. P. C. Klaver, R. Drautz, and M. W. Finnis, “Magnetism and thermodynamics of defect-free Fe–Cr alloys,” Phys. Rev. B **74**, 094435 (2006).
6. A. V. Ruban, P. A. Korzhavyi, and B. Johansson, “First-principles theory of magnetically driven anoma-

lous ordering in bcc Fe–Cr alloys,“ Phys. Rev. B **77**, 094436 (2008).

7. W. Xiong, P. Hedström, M. Selleby, J. Odqvist, M. Thuvander, and Q. Chen, “An improved thermodynamic modeling of the Fe–Cr system down to zero Kelvin coupled with key experiments,” Calphad **35**, 355–366 (2011).
8. M. I. Gol’dshtein, S. V. Grachev, Yu. G. Veksler, *Special Steels* (Mosk. Inst. Stali i Splavov, Moscow, 1999).
9. E. C. Stoner and C. P. Wohlfarth, “A mechanism of magnetic hysteresis in heterogeneous alloys,“ Philos. Trans. Roy. Soc. A **240**, 599–642 (1948).
10. B. O. Mukhamedov, A. V. Ponomareva, and I. A. Abrikosov, “Spinodal decomposition in ternary Fe–Cr–Co system,“ J. Alloys Compd. **695**, 250–256 (2017).
11. A. A. Mirzoev, M. M. Yalalov, and D. A. Mirzaev, “Calculation of the energy of mixing for the Fe–Cr alloys by the first-principles methods of computer simulation,“ Phys. Met. Metall. **103**, 83–87 (2007).
12. D. A. Mirzaev and A. A. Mirzoev, “Magnetic component of mixing enthalpy for bcc Fe–Cr alloys: ab initio based model,” J. Phys.: Conf. Ser. **1389**, 012007 (2019).
13. I. K. Razumov and I. G. Shmakov, " The model of decomposition of a Fe–Cu alloy with concentration-depending interatomic interactions,“ Phys. Solid State **61**, 952–961 (2019).
14. I. K. Razumov, Yu. N. Gornostyrev, and M. I. Katsnelson, “Towards the ab initio based theory of phase transformations in iron and steel,“ Phys. Met. Metallogr. **118**, 362–388 (2017).
15. G. Inden, “The mutual influence of magnetic and chemical ordering,“ MRS Proc. **19**, 175–188 (1982).
16. A. Kuronen, S. Granroth, M. H. Heinonen, R. E. Perälä, T. Kilpi, P. Laukkanen, J. Lång, J. Dahl, M. P. J. Punkkinen, K. Kokko, M. Ropo, B. Johansson, and L. Vitos, “Segregation, precipitation, and α–α' phase separation in Fe–Cr alloys,“ Phys. Rev. B **92**, 214113 (2015).
17. D. Nguyen-Manh, M. Yu. Lavrentiev, and S. L. Dudarev, “The Fe–Cr system: atomistic modelling of thermodynamics and kinetics of phase transformations,“ C. R. Phys. **9**, 379–388 (2008).
18. J. B. J. Chapman, P. W. Ma, and S. L. Dudarev, “Dynamics of magnetism in Fe–Cr alloys with Cr clustering,“ Phys. Rev. B **99**, 184413 (2019).
19. M. Levesque, E. Martinez, C.-C. Fu, M. Nastar, and F. Soisson, “Simple concentration-dependent pair interaction model for large-scale simulations of Fe–Cr alloys,“ Phys. Rev. B **84**, 184205 (2011).
20. W. Xiong, M. Selleby, Q. Chen, J. Odqvist, and Y. Du, “Evaluation of phase equilibria and thermochemical properties in the Fe–Cr system,” Crit. Rev. Solid State Mater. Sci. **35**, 125–152 (2010).
21. W. Xiong, J. Odqvist, P. Hedström, M. Selleby, M. Thuvander, and Q. Chen, “An improved thermodynamic modeling of the Fe–Cr system down to zero kelvin coupled with key experiments,“ CALPHAD **35**, 355–366 (2011).
22. J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon, New York, 2002). 806 c.
23. J. Strečka and M. Jaščur, “A brief account of the Ising and Ising-like models: mean-field, effective-field and exact results,” Acta Phys. Slovaca **65**, No. 4, 235–367 (2015).
24. J. M. Sanchez, “Generalized cluster description of multicomponent systems,” Physica A **128**, 334–350 (1984).
25. M. Yu. Lavrentiev, S. L. Dudarev, and D. Nguyen-Manh, J. Nucl. Mater. **386–388**, 22–25 (2009).
26. M. Yu. Lavrentiev, J. S. Wrobel, D. Nguyen-Manh, S. L. Dudarev, and M. G. Ganchenkova, “Magnetic cluster expansion model for random and ordered magnetic face-centered cubic Fe–Ni–Cr alloys,” J. Appl. Phys. **120**, 043902 (2016).
27. J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, 1968).
28. I. K. Razumov, Yu. N. Gornostyrev, and M. I. Katsnelson, “Effect of magnetism on kinetics of γ–α transformation and pattern formation in iron,” J. Physics: Condens. Matter **25**, No. 13. 135401 (2013).
29. Dzh. Zaiman, *Models of Disorder* (Mir, Moscow, 1982) [in Russian]
30. Y. Wang, H. Hou, J. Yin, S. Hu, X. Liu, F. Xue, C. H. Jr. Henager, and J. Wang, “The magnetic effects on the energetic landscape of Fe–Cu alloy: A model Hamiltonian approach,” Comp. Mater. Sci. **145**, 163–173 (2018).
31. G. Kirchner, T. Nishizawa, and B. Uhrenius, “The distribution of chromium between ferrite and austenite and the thermodynamics of the α/γ equilibrium in the Fe–Cr and Fe–Mn Systems,” Metall. Trans. **4**, 167–174 (1973).
32. H. Kaneko, M. Homma, and K. Nakamura, “Phase diagram of Fe–Cr–Co permanent magnet system,” IEEE Trans. Magn., No. 5, 1325–1327 (1977).
33. A. V. Ponomareva, A. V. Ruban, B. O. Mukhamedov, and I. A. Abrikosov, “Effect of multicomponent alloying with Ni, Mn and Mo on phase stability of bcc Fe–Cr alloys,” Acta Mater. **150**, 117–129 (2018).
34. M. L. Bernshtein et al. *Metal Science and Heat Treatment of Steel and Cast Iron*, Ed. by A. G. Rakhshtadt (Intermet Inzheniring, Moscow, 2005), vol. 2.
35. K. Binder, “Nucleation barriers, spinodals, and the Ginzburg criterion,” Phys. Rev. A **29**, 341–349 (1984).
36. D. Chandra and L. Schwartz, “Mössbauer effect study on the 475°C decomposition of Fe–Cr,” Metall. Trans. **2**, No. 9, 511–519 (1971).
37. B. Fultz, “Vibrational thermodynamics of materials,” Prog. Mater. Sci. **55**, 247–352 (2010).

Translated by O. Kadkin