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Ab initio analysis of energetics of σ-phase formation in Cr-based systems

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A theoretical approach to the explanation of experimentally determined positive enthalpy of formation in Cr-based σ phases is presented. It turns out that the energy of formation of σ phases in Cr-Co and Cr-Fe systems is found to be negative taking the pure components in the σ-phase structure as the standard states. Our treatment represents a first step to a model of an explanation of the stability of the σ phase.

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I. INTRODUCTION

In 1923 Bain[1] observed a hard and nonmagnetic phase in the Cr-Fe system, later called the σ phase. The reaction forming this phase was sluggish and the σ phase was observed even after a long-time high-temperature annealing in the Cr-Fe system near the 1:1 composition. It attracted a lot of the attention of material scientists because it is very brittle and stable and therefore its presence causes severe degradation of material properties.

The crystal structure of this phase was determined in 1943 with the help of x rays by Cook and Jones.[2] The repeat cell consists of 30 atoms arranged in 5 crystallographically inequivalent sublattices.[3–5] Similar σ phases were observed also in other ($\sim$40) systems such as, e.g., Cr-Co, Cr-Mn, Fe-V, etc.

The reason why this structure is formed is not obvious at first glance. In the calorimetric studies of various authors, positive values of the enthalpy of formation H_{form} of the σ phase in both Cr-Fe and Cr-Co systems were reported.[6–9] The enthalpy of formation H_{form} represents the change in the Gibbs energy G_{form} at $T=0$ K. If we neglect the temperature dependence of H_{form}, which is usually very well justified in metallic systems, its positive value means that the σ phase should not be stable at 0 K relative to the phases used as standard states, which were really existing structures of the constituent elements in all cases mentioned (ferromagnetic hcp for Co, antiferromagnetic bcc for Cr, and ferromagnetic bcc for Fe). It may be expected that entropy contributions are responsible for the σ-phase formation at higher temperatures. The stability of any solid phase at $T\neq 0$ K is governed by the Gibbs energy

$$G=E_{tot}+PV-TS, \tag{1}$$

where E_{tot} is the calculated total energy of the phase and S is the sum of configurational and vibrational entropy (the changes in the product of pressure and volume may be neglected in the present considerations). The stability of the σ phase in some temperature interval $\langle T_1,T_2\rangle$ (these temperatures may be found in the corresponding phase diagram) follows then from the fact that the Gibbs energy of any other phase is higher than the Gibbs energy of the σ phase. Configurational entropy is, at a given concentration, constant in the σ phase. However, vibrational entropy increases with temperature, but differently in different phases. Therefore, the relative stability of the σ phase could increase at lower temperatures, due to a positive value of the configurational entropy S_{config} and a decrease at higher temperatures, due to a steeper increase of the vibrational entropy S_{vibr} in coexisting phases.

II. ELECTRONIC STRUCTURE CALCULATIONS

To explain experimentally determined heat of formation of the σ phase, we must know which combinations of occupancies of sublattices in the σ-phase structure are the most stable ones at a given concentration and, therefore, which total energies should be compared with the calorimetric data. For this purpose we performed first-principles electronic structure calculations of total energies for all possible 32 configurations occurring in the σ-phase structure of the systems studied.

The total energies of the Cr-Fe and Co-Cr σ phases as well as of the pure constituents in the σ phase were computed by means of the linear muffin-tin orbital method in the atomic sphere approximation[10] (LMTO-ASA) using the code by Krier *et al.*[11] The exchange-correlation energy was evaluated within the generalized gradient approximation (GGA).[12] We have used the spd basis with the f states incorporated by the downfolding procedure and with the combined-correction term included.[10,11] This is apparently the best performance the LMTO-ASA method may provide. We utilized 512 k points in the Brillouin zone. Similarly as in Ref. 13 the lattice parameters of the tetragonal σ phase and cell internal coordinates were held fixed at the experimental values for all configurations. For the Cr-Fe system we used $a=8.797$ Å, $c=4.558$ Å (Ref. 3), for the Co-Cr system $a=8.810$ Å, $c=4.560$ Å (Ref. 14). For the σ phases of the pure elements, we employed the lattice parameters of the Cr-Fe σ phase; the atomic volume of the Cr-Co σ phase is only by 0.34% higher than that of the Cr-Fe. As the Cr-Fe and Co-Cr σ phases are nonmagnetic, all calculations were performed as non-spin-polarized. Nonmagnetic pure constituents in the σ phase were used as one set of reference (standard) states.

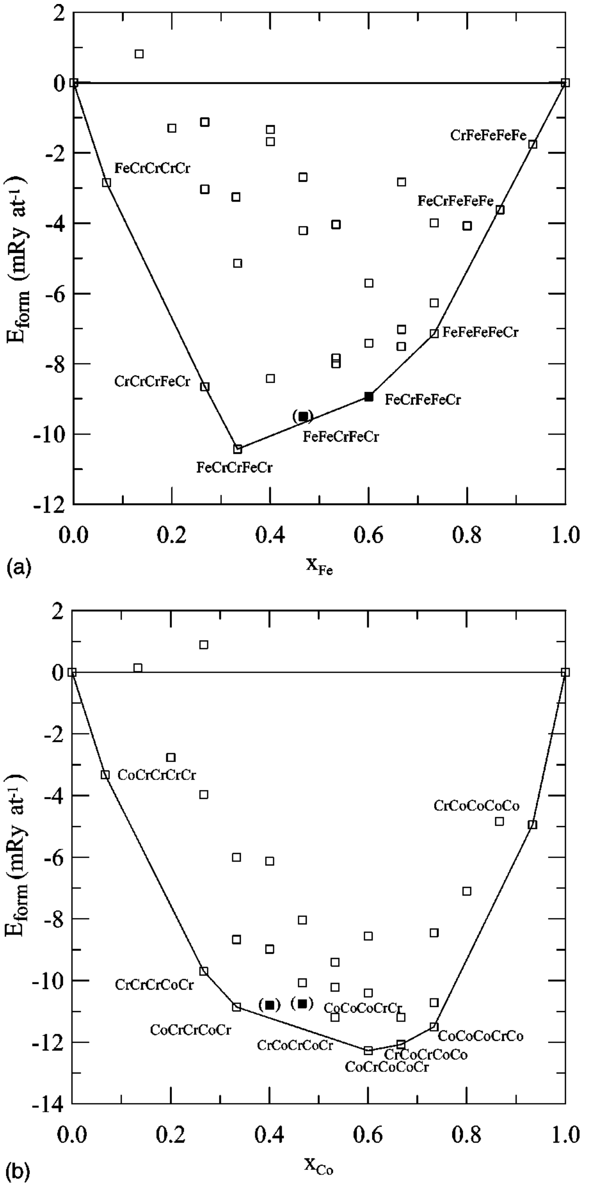

FIG. 1. Calculated formation energies of the σ phase with various occupancies of sublattices: (a) Cr-Fe, (b) Cr-Co. The most stable configurations in the region of existence of the σ phase are denoted by the solid squares. Here the hypothetical σ-phase structures of pure constituents are taken as standard states. The occupation of sublattices is given in the same order as in Table I, i.e., 2(a), 4(f), $8(\mathrm{i}_1)$, $8(\mathrm{i}_2)$, 8(j).

III. RESULTS AND DISCUSSION

Various combinations of the occupancy of five different sublattices by constituent atoms were taken into account. The formation energies (E_{form}) of Cr-Fe and Cr-Co σ phases were computed subtracting the concentration-weighted total energies of pure constituents in the σ phase from the total energies of σ-phase alloys (Fig. 1). The most stable combinations of occupation of sublattices at $T=0$ K have the lowest value of formation energy for a given composition of Cr-Fe and Cr-Co alloys and should constitute a convex region because the hypothetical σ-phase structure, taken as standard state, is less stable (has a higher G) than those structures at intermediate composition. The σ phase in $\mathrm{Cr}_{1-x}\mathrm{Fe}_x$ and $\mathrm{Cr}_{1-x}\mathrm{Co}_x$ systems was experimentally observed for $0.48<x<0.58$ (Cr-Fe) and for $0.32<x<0.46$ (Cr-Co).[15] Regrettably, the minimum energies for these concentrations [solid squares in Figs. 1(a) and 1(b)] lie slightly above the lines delimiting the convex region in the E_{form}-x plane. This is especially manifested for the Co-Cr system [Fig. 1(b)]. The reason for this may be in numerical inaccuracies of the calculated total energies. However, the points corresponding to FeFeCrFeCr in Fig. 1(a) and to CrCoCrCoCr and CoCoCoCrCr in Fig. 1(b) are only slightly above the lines delimiting the convex region and, in the following analysis, we will employ the energy values corresponding to the solid squares in Figs. 1(a) and 1(b).

TABLE I. Relative occupations y_i [$i=2(\mathrm{a})$, 4(f), $8(\mathrm{i}_1)$, $8(\mathrm{i}_2)$, 8(j)] of inequivalent lattice sites in $\mathrm{Cr}_{1-x_{\mathrm{Fe}}}\mathrm{Fe}_{x_{\mathrm{Fe}}}$ and $\mathrm{Cr}_{1-x_{\mathrm{Co}}}\mathrm{Co}_{x_{\mathrm{Co}}}$ σ phases.

Cr-Fe

	y_i					
x_{Fe}	2(a)	4(f)	$8(\mathrm{i}_1)$	$8(\mathrm{i}_2)$	8(j)	Ref.
0.508	0.88	0.25	0.38	0.84	0.34	3
0.517	0.90	0.30	0.413	0.875	0.275	3
0.525	0.90	0.285	0.40	0.85	0.35	3
0.56	0.70	0.45	0.55	0.65	0.50	15
0.567	0.60	0.45	0.60	0.65	0.50	3
0.47	1.00	1.00	0.00	1.00	0.00	12
0.47	1.00	1.00	0.00	1.00	0.00	This work
0.60	1.00	0.00	1.00	1.00	0.00	This work

Cr-Co

	y_i					
x_{Co}	2(a)	4(f)	$8(\mathrm{i}_1)$	$8(\mathrm{i}_2)$	8(j)	Ref.
0.33	1.00	1.00	0.00	0.00	0.50	3
0.39	0.65	0.05	0.15	0.625	0.50	15
0.40	0.00	1.00	0.00	1.00	0.00	This work
0.47	1.00	1.00	1.00	0.00	0.00	This work

The calculated occupations of inequivalent lattice sites in the Cr-Fe and Cr-Co σ phases are given in Table I. The differences between the calculated values and experimental results[3,16] encountered in Table I are partly due to the fact that we were not able to include the effect of the partial occupancy of individual sublattices in our LMTO-ASA calculations.

It should be emphasized that the calculated values of formation energies (where the total energies of the σ-phase structures of Fe, Co, and Cr atoms are taken as standard states) have negative values. This is, however, due to the choice of the standard states. To be able to compare our results with experimental data, the formation energies must be determined with respect to the true ground states of the constituent elements. As the LMTO-ASA method does not provide reliable structural energy differences for structures of different symmetry, we have performed, using the

TABLE II. Total energy differences ΔE between the σ phases and experimentally observed ground states for pure constituents using the FLAPW-GGA approach. The atomic volume of the elements in the σ phase is equal to the experimental atomic volume of the Cr-Fe σ phase; the total energies of the ground states are calculated at the corresponding experimental lattice parameters. The energies are given in mRy/atom; FM and AFM stand for ferromagnetic and antiferromagnetic ordering, respectively.

Element	Phases	ΔE
Co	σ-(hcp-FM)	34.4
Cr	σ-(bcc-AFM)	15.4
Fe	σ-(bcc-FM)	30.9

full-potential linearized augmented plane waves (FLAPW) method[17] and the WIEN97 code,[18] calculations of the total energy of Co, Cr, and Fe in their experimentally observed structures (at the measured lattice parameters) and in the σ-phase structure (employing the lattice parameters of the Fe-Cr σ phase exactly in the same way as in the LMTO-ASA calculations—see the end of Sec. II). In order that the comparison with the LMTO-ASA energy differences for σ phases be legitimate, we used the same GGA exchange correlation functional[12] and the same density of k points. The calculated energy differences are shown in Table II.

On the basis of the FLAPW calculations we could obtain the formation enthalpies of σ phases with respect to the ground states of constituent elements as standard states [Figs. 2(a) and 2(b)]. The resulting values (Table III) are positive which is found in most of calorimetric experiments.[6–9]

It may be seen from Figs. 3(a) and 3(b) that the experimental values of heats of formation are strongly scattered. This is connected to the difficult reproducibility of the calorimetric measurements. Although such measurements are usually very precise (typical error is lower than 5%), their reproducibility depends on many factors (such as, e.g., hidden chemical reactions, surface phenomena, kinetics of calorimetric processes, etc.) which cannot be controlled well. That is why the values for the Cr-Fe system lie within the range of 3 kJ/mol, for the Co-Cr system even in the range of 10 kJ/mol, and it is not excluded that they are influenced by some additional systematic error. Taking these facts into account, the agreement of the calculated and experimental results may be considered as quite satisfactory and encouraging.

In the future, we plan to employ first-principles calculations as a basis for modeling the composition dependence of the Gibbs energy of intermetallic phases in the CALPHAD (calculation of phase diagrams based on thermochemical data) method. Nowadays, such a modeling is performed using the assumption that the atoms are ordered on two or more sublattices.[4,19] The problem consists in the dilemma into which sublattice each element goes and, further, how to reduce the number of sublattices in modeling in order to restrict the number of model parameters. For binary A-B systems (A being an element of the VIth group of the periodical table or lower, B being an element of the VIIth group or higher), a guideline for reducing the number of sublattices was proposed as follows.[19]

TABLE III. Calculated formation energies E_{form} of the σ phases in $Cr_{1-x}Fe_x$ and $Cr_{1-x}Co_x$ (stable structures of the constituent elements are taken as standard states). The values in the table correspond to the arrows in Figs. 2 and 3.

System	x	E_{form} (kJ/mol)
Cr−Fe	0.47	16.78
	0.60	20.28
Co−Cr	0.40	15.32
	0.47	17.56

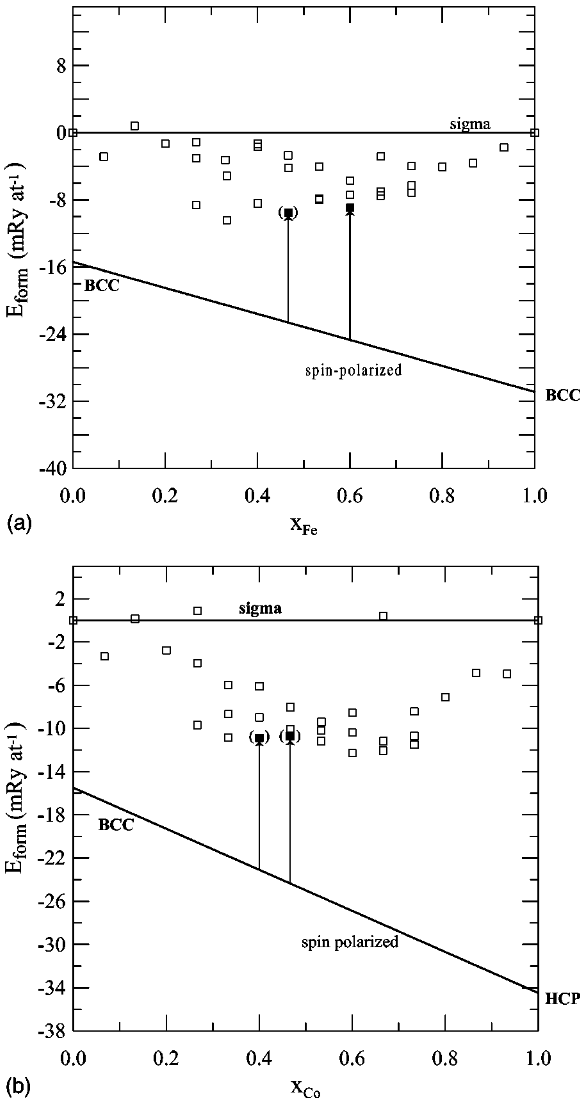

FIG. 2. Calculated formation energies of the σ phase: (a) Cr-Fe, (b) Cr-Co. The most stable configurations in the region of existence of the σ phase are denoted by the solid squares. Here, again, the hypothetical σ-phase structures of pure constituents are taken as standard states. The arrows starting at the straight line connecting the bcc Cr and Fe (a) or bcc Cr and hcp Co (b) states show the formation energies with respect to the real standard states.

(i) Combine all sublattices with the same coordination number (CN) and similar point symmetry into one.

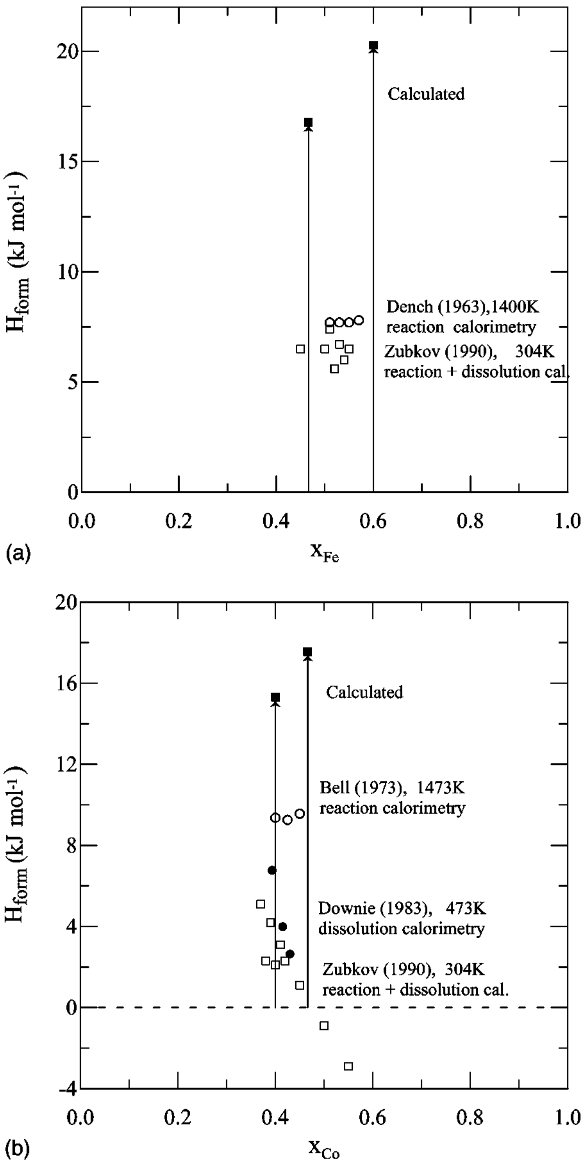

FIG. 3. Calorimetricaly determined enthalpies of formation of σ phases compared with the calculated formation energies: (a) Cr-Fe, (b) Cr-Co. Here experimentally observed structures of pure constituents are taken as the standard states.

(ii) If more than one remain, combine the two with the highest CN into one.

(iii) Arrange the reduced set of sublattices in the order of increasing CN.

(iv) B elements will go preferentially into the first sublattice but it may dissolve some A.

(v) The next sublattice will be preferentially filled with A but it may dissolve some B.

(vi) If there is a third sublattice, it will be reserved for A.

As an example, for the σ phase the following formula was obtained: $(A,B)_{10}(A,B)_{16}A_4$.[19] However, the above-mentioned procedure of modeling has no exact physical background. It only enables us to estimate the lattice stability of a metastable phase by means of known the Gibbs energies of stable phases of pure constituents with the same coordination number. Using this approach, we are able to express the Gibbs energy of pure constituents in the σ phase, but this Gibbs energy has to be adjusted to phase equlibrium data and, therefore, its physical reliability is questionable. Further, it is known from x-ray studies[16] that the mixing of the constituents takes place at all sublattices. The CALPHAD model proposed in Ref. 19 does not respect this fact.

Electronic structure calculations could bring a substantial improvement of that model. Namely, knowledge of a correct value of the total energy difference between the σ phase and the usual (stable structure) standard state of pure elements from first principles enables us to build up the Gibbs energy of the σ phase of pure elements on a physically correct energetical base and only the entropic term must be adjusted to phase equilibrium data. Subsequently, the values of the Gibbs energy for continually variable compositions of the real (alloy) σ phase could be calculated by interpolation of the results obtained for some specific composition (such as, e.g., in this study). Thus, this approach will provide a reliable physical background and considerable simplification of the modeling of the thermodynamic properties of the σ phase in the CALPHAD method.

IV. CONCLUSIONS

The first-principles calculations presented in this work provide a deeper understanding of the role of standard states in a thermodynamic description of ordered structures and enable us to gain insight into the processes of phase formation. The agreement of the calculated total energy differences between the σ phase and other relevant phases of Cr, Co, and Fe with experimentally measured enthalpies of formation of the σ phase constitutes a reliable basis for further similar calculations. These first-principles calculations should be the first step to determine the stability of various structures and to assess the formation of unwanted phases, damaging the properties of materials.

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