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# Ab Initio Calculations of Phase Stabilities in the Fe-Al-C System and CALPHAD-Type Assessment of the Iron-Rich Corner

P. MAUGIS, J. LACAZE, R. BESSON, and J. MORILLO

The goal of this article is to improve the description of the Fe-Al-C phase diagram through the density-functional theory (DFT) calculation of the  $\text{Fe}_3\text{AlC}$  compound. Several binary stoichiometric compounds in the iron-rich part of the ternary Fe-Al-C system and the ternary stoichiometric carbide  $\text{Fe}_3\text{AlC}$  are studied *ab initio*. The results in terms of lattice parameter, bulk modulus, magnetization, and enthalpy of formation are compared with the calculated values available in the literature. *Via* a fitted entropy of formation of the ternary carbide, the Gibbs energy of formation of this compound is evaluated as a function of temperature. A CALPHAD-type procedure is then used to calculate ternary Gibbs isotherms at 800 °C, 1000 °C, and 1200 °C. The isotherms are compared with the experimental data of the literature.

## I. INTRODUCTION

IT has been largely reported that aluminum-alloyed steels can be hardened by a dispersion of  $\kappa$ - $\text{Fe}_3\text{AlC}$  carbides (*e.g.*, References 1 through 3) and the microstructure of such steels has been investigated in detail<sup>[4,5,6]</sup> (Figure 1). However, to control the precipitation microstructures of steels and also to master the carburizing process of Fe-Al alloys, it is necessary to rely on the thermodynamical properties of the iron-rich phases in the Fe-Al-C system. As a matter of fact, if such thermodynamics have been studied in high Mn-containing steels,<sup>[6,7]</sup> no detailed description of this part of the Fe-Al-C phase diagram is available in the literature. The perovskite  $\kappa$ - $\text{Fe}_3\text{AlC}$  carbide, in particular, is hardly known. Partial information has been published: Palm and Inden have investigated experimentally specific Gibbs isotherms of the Fe-Al-C system,<sup>[8]</sup> and recently, Ohtani *et al.*<sup>[9]</sup> published a Fe-Al-Ni-C phase diagram based on *ab initio* calculations.

It is the purpose of this article to provide some information on the stability of the  $\kappa$  phase by means of *ab initio* calculations. Use of the calculation of phase diagrams (CALPHAD) approach<sup>[10]</sup> is made for the construction of the Fe-Al-C phase diagram.

## II. COMPUTATIONAL DETAILS

The *ab initio* calculations are based on the density-functional theory (DFT).<sup>[11,12]</sup> They are performed with the Vienna *Ab Initio* Simulation Package VASP 4.6,<sup>[13,14,15]</sup> implementing the projector augmented wave (PAW) method.<sup>[16,17]</sup> The Perdew–Burke–Ernzerhof (PBE)<sup>[18]</sup> gen-

eralized gradient approximation (GGA) for the exchange and correlation functional in its spin-polarized version was used. The PAW pseudopotentials correspond to the  $3d^6 4s^2$  (Fe),  $3s^2 3p^1$  (Al), and  $2s^2 2p^2$  (C) valence electron configurations. Local magnetic moments on iron were calculated by integrating the magnetization densities within atom-centered spheres with a radius of 1.3 Å.

The supercell approach with periodic boundary conditions was used to simulate the different phases. Brillouin-zone sampling was performed using the Monkhorst–Pack scheme<sup>[19]</sup> with a grid centered on the  $\Gamma$  point. For all phases, except diamond carbon, the density of  $k$  points was chosen in the order of 5000  $k$  point  $\times$  atom. For these phases, the plane-wave energy cutoff is 400 eV. Diamond carbon necessitated a higher cutoff (800 eV) but a smaller density of  $k$  points (1500  $k$  point  $\times$  atom). Lattice parameters and atomic positions were relaxed using the standard conjugate gradient algorithms implemented in the VASP code. The chosen energy cutoff,  $k$  points, and convergence parameters were checked to ensure a convergence in energy of the order of 1 meV per atom.

The formation enthalpies at 0 K are calculated taking as reference the following pure phases: bcc ferromagnetic iron, fcc aluminum, and graphite. However, as graphite is not reliably modeled in the DFT approach, the diamond structure of carbon has been calculated instead. The enthalpy of graphite has been taken equal to that of diamond minus the enthalpy difference of 1.895 kJ/mol tabulated in References 20 and 21. We use the convention that the formation enthalpy is negative for a stable phase and positive in the opposite case. Enthalpies are given in kJ per mole of atoms.

## III. RESULTS OF THE AB INITIO CALCULATIONS

### A. Pure Elements

*Ab initio* calculation of the pure elements in their stable form is needed as a reference for the evaluation of the formation enthalpy of the compounds formed from these elements. The results of the calculations of bcc ferromagnetic iron, fcc aluminum, and diamond carbon are given in Table I. The calculated values are within 1 pct of the

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literature data measured at room temperature. One exception is the bulk modulus of iron, which is calculated 15 pct higher than the literature value.

### B. Binary Compounds

The binary compounds  $\text{Fe}_3\text{C}$ , B2-FeAl,  $\text{D0}_3\text{-Fe}_3\text{Al}$ , and  $\text{L1}_2\text{-Fe}_3\text{Al}$  have been studied. The results of the calculations are briefly described here and compared with the literature data. These compounds are also intended for reference to study the effect of carbon incorporation in some Fe-Al alloys.

The crystal structure of cementite  $\text{Fe}_3\text{C}$  consists of 4 carbon atoms and 12 iron atoms distributed on an orthorhombic lattice and resulting in a 16-atom primitive cell.\*

\*Pearson symbol oP16, Strukturbericht designation  $\text{D0}_{11}$ .

There are two types of sites for the iron atoms. Both experimental results<sup>[22,23]</sup> and LMTO calculations<sup>[24]</sup> report the ferromagnetism of the phase and the magnetic moments of the iron atoms. Our calculations are in agreement with these results. The formation enthalpy of cementite is found to be positive, which is consistent with the fact that cementite is metastable relative to bcc iron and graphite. The

difference between our calculated value of 10.9 kJ/mol and the value of 6.276 kJ/mol reported in the thermodynamic database of SGTE<sup>[21]</sup> is in the range of the usual absolute uncertainty of about 4 kJ/mol on both calorimetric measurements and *ab initio* calculations.

The FeAl phase orders at low temperature in the B2 structure on the bcc lattice. Calculations have been performed on the stoichiometric compound. Our result of  $-32.2$  kJ/mol for the formation enthalpy agrees within  $\pm 15$  pct, with the values obtained by Lechermann<sup>[25,26]</sup> and Gonzales<sup>[27]</sup> with other DFT techniques (Figure 2). It is in the range of the calorimetric results that span from  $-24$  to  $-40.5$  kJ/mol (Reference 28).

We have calculated two crystalline forms of the  $\text{Fe}_3\text{Al}$  stoichiometric compound. The stable structure is reported as  $\text{D0}_3$ , ordered on the bcc lattice and counting 16 atoms in the conventional cell. There are two sets of equivalent sites for the iron atoms. Our calculated lattice parameters and magnetic moments are very close to those calculated by Lechermann in FLAPW-PBE.<sup>[29]</sup> Our calculations yield a formation enthalpy of  $-19.3$  kJ/mol. For comparison, Lechermann with FLAPW finds  $-18.9$  kJ/mol in LSDA and  $-21.2$  kJ/mol in GGA. Gonzales<sup>[27]</sup> with FLAPW finds  $-21.5$  kJ/mol in the GGA approximation. Our result is in the range of the preceding literature results. It lies in the

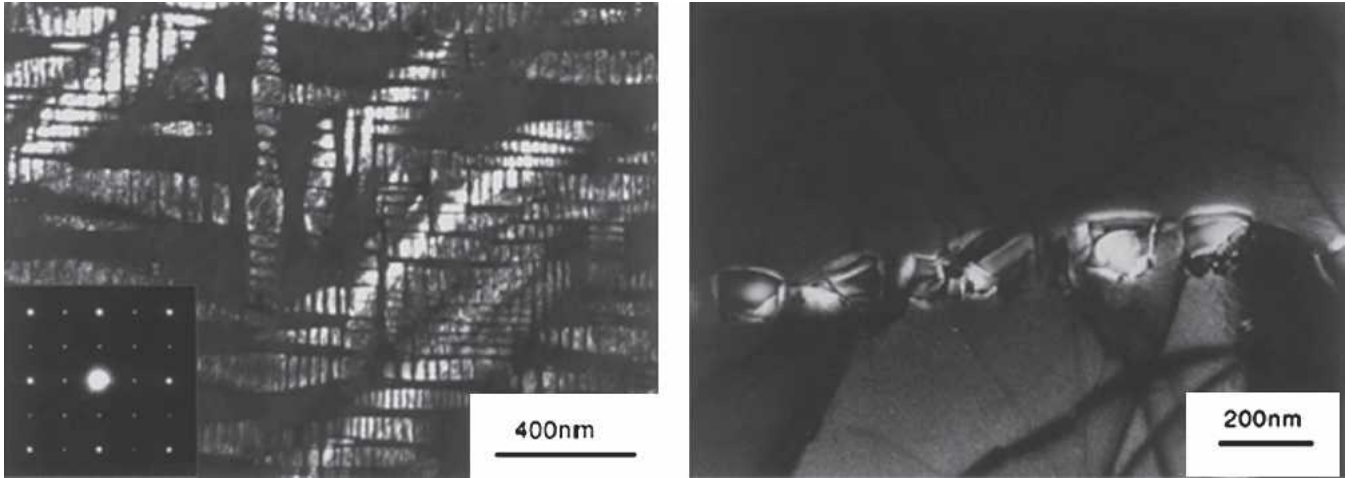


Fig. 1— $\kappa$  phase precipitated in an austenitic matrix. Intragranular (left) and intergranular (right) precipitates. Dark-field TEM images after Li.<sup>[6]</sup>

**Table I. Results of the Calculations; the Magnetic Moments are Given for Each Set of Equivalent Iron Atoms; for the Orthorhombic  $\text{D0}_{11}$  Structure, the Lattice Parameters  $a$ ,  $b$ , and  $c$  are Reported**

Compound	Crystal Structure	Lattice Parameters (nm)	Atomic Volume ( $10^{-3} \text{ nm}^3$ )	Bulk Modulus (GPa)	Magnetic Moment ( $\mu_B/\text{at. Fe}$ )	Formation Enthalpy (eV/at.)	Formation Enthalpy (kJ/mol at.)
Fe	bcc	0.283	11.38	197	2.20	0	0
Al	fcc	0.404	16.47	78	0	0	0
C	diamond	0.357	5.70	433	0	+0.020	+1.90
$\text{Fe}_3\text{C}$	$\text{D0}_{11}$	0.447/0.503/0.671	9.43	n.c.	1.95/1.86	+0.113	+10.9
FeAl	$\text{B}_2$	0.288	11.88	177	0.71	-0.334	-32.2
$\text{Fe}_3\text{Al}$	$\text{D0}_3$	0.574	11.81	174	2.39/1.89	-0.200	-19.3
$\text{Fe}_3\text{Al}$	$\text{L1}_2$	0.365	12.14	158	2.35	-0.200	-19.3
$\text{Fe}_3\text{AlC}$	$\text{L}'1_2$	0.375	10.56	n.c.	1.12	-0.188	-18.2

n.c., not calculated.

range of the calorimetric results, which are widely scattered from  $-14$  to  $-31$  kJ/mol.

The  $L1_2$ - $Fe_3Al$  structure is ordered on the fcc crystal lattice, containing 4 atoms per cell. It is not part of the experimental binary phase diagrams.<sup>[30,31]</sup> The  $L1_2$  structure is calculated here for comparison with the related  $E2_1$  perovskite structure of the  $\kappa$  phase. Again, our results are very close to those calculated by Lechermann in FLAPW-PBE.<sup>[29]</sup> The formation enthalpy of  $L1_2$ - $Fe_3Al$ ,  $-19.3$  kJ/mol, is found to be equal to that of the stable  $D0_3$ - $Fe_3Al$  within the uncertainty of the method. This result has been previously discussed by Lechermann,<sup>[29]</sup> who points out the influence of the calculation approximations on the relative stabilities of the two phases.

### C. The Ternary $\kappa$ - $Fe_3AlC$ Compound

The ternary  $Fe_3AlC$  compound is ordered in the perovskite structure.\* Its crystal structure can be seen as a  $L1_2$ -

\*Pearson symbol cP5, Strukturbericht designation  $L1_2$  or  $E2_1$ .

$Fe_3Al$  compound with a carbon atom lying in the center of the cubic cell in octahedral position relative to the iron atoms (Figure 3). Because of the radius of the carbon atom, the  $Fe_3AlC$  structure is inflated and somewhat energetically destabilized. According to Palm,<sup>[8]</sup> this is the reason why the *stoichiometric* compound is not stable relative to cementite, ferrite, or austenite. In fact, the  $\kappa$  phase is often

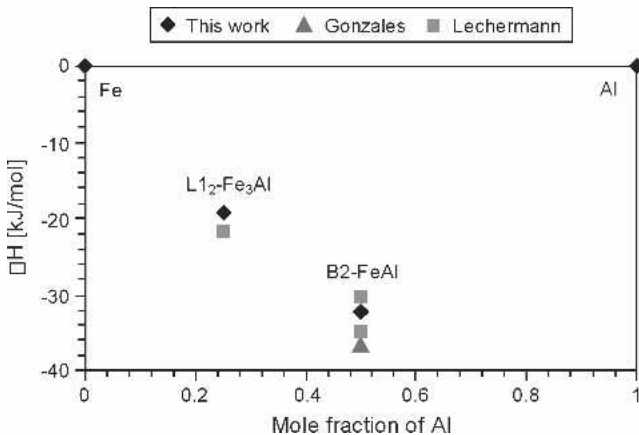


Fig. 2—Formation energies of various compounds in the Fe-Al system. Our calculations agree within  $\pm 4$  kJ/mol with the DFT calculations of Gonzales<sup>[27]</sup> and Lechermann.<sup>[29]</sup>

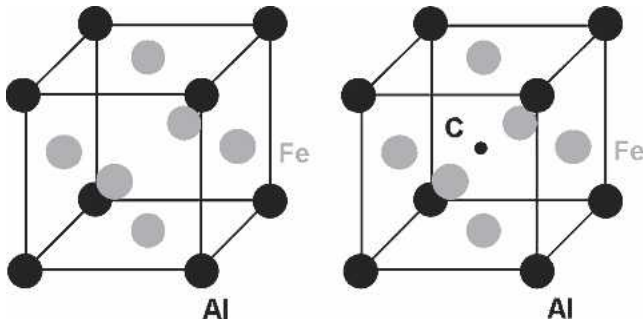


Fig. 3—The  $L1_2$  structure of  $Fe_3Al$  (left) and the perovskite  $E2_1$  structure of  $Fe_3AlC$  (right).

reported as understoichiometric in carbon, with a typical composition of  $Fe_3AlC_{0.5}$ . As preliminary results, we report here calculations on the stoichiometric compound only. The effects of nonstoichiometry are under investigation and will be reported in a future publication.

The results of our calculations are given in Table II. The calculated lattice parameter is 0.375 nm. As expected from the steric hindrance of the carbon atom, the lattice parameter of  $\kappa$ - $Fe_3AlC$  is significantly larger than that of  $L1_2$ - $Fe_3Al$  (0.365 nm). The stable structure is ferromagnetic at 0 K with a magnetic moment of  $1.12 \mu_B$  on the three equivalent iron atoms. This value is small compared to the one associated with the  $L1_2$ - $Fe_3Al$  compound. Very few data are available in the literature for direct comparison of our results (Table II). Our lattice parameter is close to the value of 0.378 nm reported in *Pearson's Handbook*.<sup>[32]</sup>

The key result of this work is the enthalpy of formation of the ternary carbide. We find  $-18.2$  kJ/mol, or equivalently  $-90,850$  J, for one mole of  $Fe_3AlC$ . The only published value to which this is comparable was calculated recently by Ohtani.<sup>[9]</sup> The authors used the FLAPW method in the GGA approximation with the WIEN2k package. They report  $-27.9$  kJ/mol. The discrepancy with our result is of the order of 10 kJ/mol, or equivalently  $+50$  pct in absolute value. Such a high discrepancy is rather unexpected. In fact, our calculations on the binary compounds show an uncertainty of less than  $\pm 2$  kJ/mol, or equivalently  $\pm 10$  pct, between our VASP calculations and the calculations of Lechermann<sup>[29]</sup> and of Gonzales<sup>[27]</sup> with, respectively, the WIEN2k and WIEN97 software.

## IV. THE CALCULATED PHASE DIAGRAM

We used the CALPHAD approach<sup>[10]</sup> for the construction of the Fe-Al-C phase diagram. The Thermo-Calc version M software was used to compute the phase equilibria. The database was SSOL for all phases except for the  $\kappa$  carbide. The Gibbs energy of formation of the  $\kappa$  carbide  $\Delta G(T)$  has been introduced in the database. Evaluation of  $\Delta G(T)$  was done with the following method.

The *ab initio* calculations yielded the enthalpy of formation of one mole of the  $\kappa$  carbide at 0 K according to the reaction  $3Fe + Al + C \leftrightarrow Fe_3AlC$ :  $\Delta_f H = -90,850$  J. We made the usual assumption that  $\Delta_f H$  is independent of temperature. We assumed further that the entropy of formation  $\Delta_f S$  is independent of temperature. Then, the Gibbs energy of formation writes  $\Delta_f G(T) = \Delta_f H - T \Delta_f S$ . We incorporated this formula in the SSOL database. Thermo-Calc calculations allow for the determination of ternary isotherms.

Table II. Results of the Calculations for the  $\kappa$ - $Fe_3AlC$  Stoichiometric Compound and Comparison with Literature Data

	This Work	Experimental <sup>[32]</sup>	Calculation <sup>[9]</sup>
Lattice Parameter (nm)	0.375	0.378	—
Magnetization ( $\mu_B$ /at Fe)	1.12	—	—
Formation enthalpy (eV/at.)	-0.19	—	-0.29
Formation enthalpy (kJ/mol)	-18.2	—	-27.9

The unknown entropy of formation has been fitted to the experimental isotherms of Palm.<sup>[8]</sup> The best fit is obtained with  $\Delta_f S = 3.54 \text{ J} \cdot \text{K}^{-1}$  for one mole of the  $\kappa$  carbide. The resulting isotherms at 800 °C, 1000 °C, and 1200 °C are shown in Figure 4 and compared with the experimental ones.

The agreement is qualitatively good: except for the higher temperature of 1200 °C, the topology of the phase diagrams are equivalent. This is an encouraging result. The solubility limits, however, are quantitatively different. One reason is that we have restricted our description to the *stoichiometric* carbide, whereas it is clear in Figure 4 that a rather large composition domain exists for this phase. Therefore, the surface of the Gibbs energy is restricted to a single point and the absolute value of  $\Delta_f G(T)$  is probably underestimated. The second reason is not specific to the  $\kappa$  phase but relates to ferrite and austenite: an improvement will certainly arise from a better description of carbon and aluminum in the solid solutions. Note that the calculated diagrams refer to equilibria with cementite, whereas the

experimental diagrams are with graphite. This results in slight modifications of the solubility limits, but does not account for the main discrepancies.

## V. CONCLUSIONS

We have studied several compounds in the iron-rich corner of the Fe-Al-C system in the framework of the DFT. Our results on the binary systems agree well with the literature results obtained with similar approaches. The formation enthalpy of the ternary stoichiometric  $\kappa$  carbide, however, is significantly different from the value published in the literature. Further investigation is needed to understand this point. Using the CALPHAD approach, we have fitted the entropy of formation of the carbide. We find a Gibbs energy of formation  $\Delta_f G(T) = -90,850 - 3.54 T$  for one mole of  $\text{Fe}_3\text{AlC}$ . This value allows for the construction of Gibbs isotherms that agree qualitatively with the published experimental phase diagram.

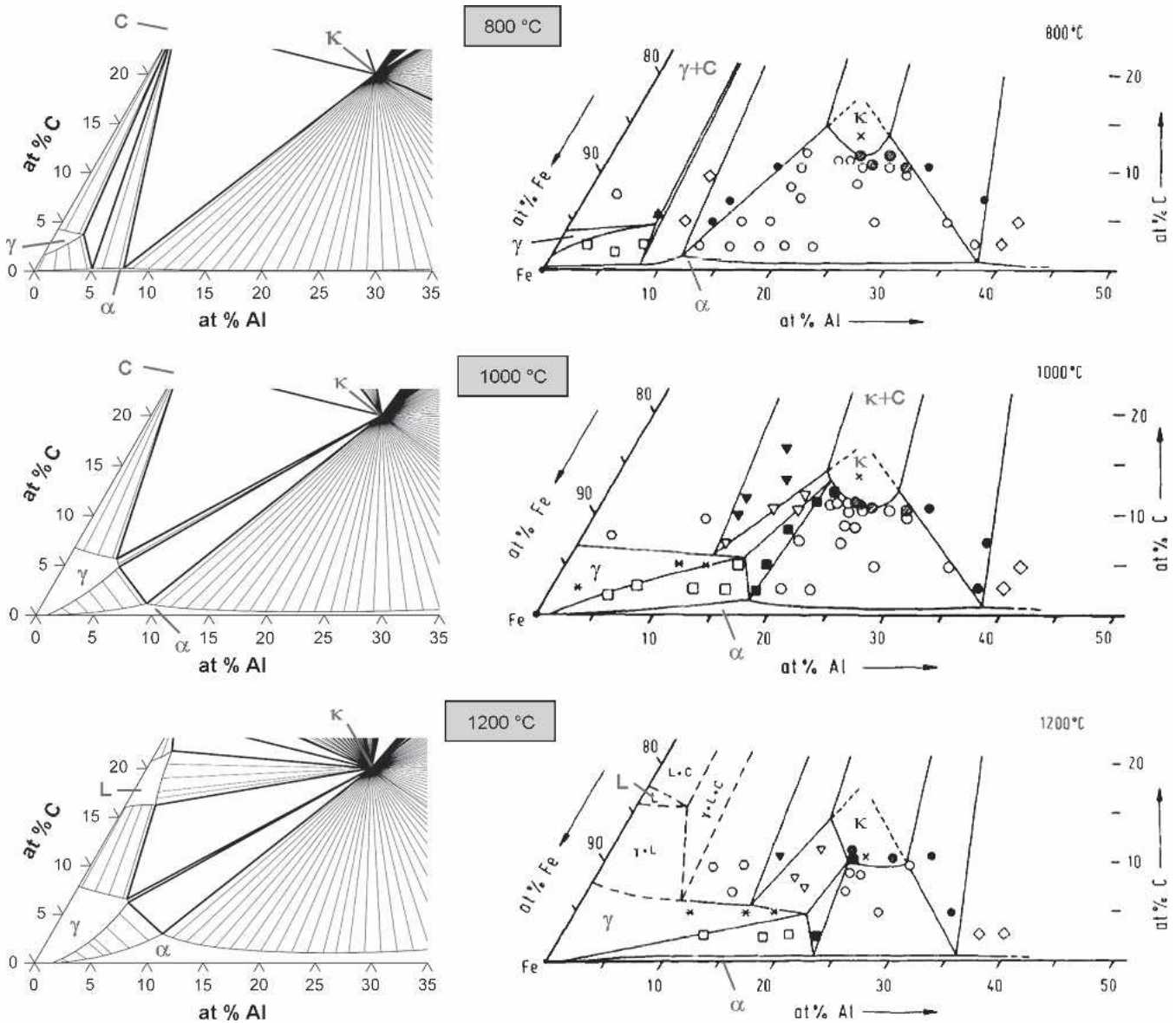


Fig. 4—Our calculations (left column) of three Gibbs isotherms reproduce qualitatively the topology of the experimental isotherms of Palm<sup>[8]</sup> (right column).

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