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Distribution of interstitials in fcc iron-carbon austenite: Monte Carlo simulations versus Mössbauer analysis

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A study of the distribution of carbon atoms in the octahedral interstitial sites of the face-centered-cubic (fcc) austenite phase in iron-carbon alloys combines an analysis of the chemical potential of C, based on the quasichemical approximation to the statistical mechanics of interstitial solutions, with three-dimensional Monte Carlo simulations and Mössbauer results. The simulations are performed using a C-C interaction energy extracted from available activity data by assuming a gas like mixture of C atoms and vacancies (V) in the octahedral interstitial sites. The number of C-C atom pairs, as well as C-V and V-V pairs, are calculated and compared with those given by the quasichemical model. Furthermore, the relative fraction of the various Fe environments are calculated and compared with those extracted from the Mössbauer spectra. The simulations reproduce well the relative fractions obtained from Mössbauer spectra assuming the Fe_8C_{1-x} model, which includes some blocking of the nearest neighbor interstitial sites by a C atom. With the information obtained in the present study, a critical discussion is reported of the extent to which such blocking effect is accounted for in the current thermodynamic models of the Fe-C fcc phase.

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I. INTRODUCTION

The physical properties of the austenite phase in the Fe-C system have been studied extensively over the years in connection with, e.g., the assessment and understanding of the phase diagram,[1–6] and the diffusion controlled[7] and the martensitic phase transitions in Fe-C alloys.[8] In austenite the iron atoms are arranged in a close-packed face-centered-cubic (fcc) lattice, and the C atoms occupy a limited number of the crystallographically equivalent octahedral interstices, which are located at the centers and at the midpoints of the edges of the cubic unit cells.[9] Models of austenite are based on considering two sublattices: one for the Fe atoms, and the other for the mixture of carbon atoms (C) and vacant octahedral interstices (V). The general theme of the present paper is the distribution of the C atoms in the interstitial sites, as revealed by three complementary sources of information, viz., thermodynamic properties, Mössbauer measurements, and Monte Carlo simulations.

If austenite were an ideal solution, C and V would distribute themselves at random in the octahedral interstitial sites, the number of which is equal to that of Fe atoms. The thermodynamic activity (a_c) of C in such an ideal mixture of N_C carbon atoms with N_{Fe} iron atoms is shown to be proportional to the ratio $y/(1-y)$, where $y=N_C/N_{Fe}$ represents the fraction of occupied interstitial sites.[10–13] Since the measured a_c in austenite deviates positively from ideal solution model, many approaches have been proposed to account for the experimental, nonideal behavior.[14–22] The reader is referred to Ref. 23 for a recent review of the work of most relevance for the present study. In the strict version of the approach known as the hard-blocking excluded-sites model (HBESM) it is assumed that the presence of a solute atom blocks a certain number (b) of the nearest neighbor interstitial sites (NIS's), so that a site is either blocked or is available for the mixing of C atoms and V.[9,14,23] Further, if the mixing in the nonblocked sites occurs at random, the activity a_c in austenite becomes proportional to $y/\{1-(b+1)y\}$.[23] Frequently, b has been treated as an adjustable parameter, identified with the value to be inserted in the expression for a_c in order to reproduce the experimental data.[9,19,21,23] Alternatively, some theoretical studies have suggested that b should in fact be treated as composition dependent.[18,21] In the present work a different approach based on combining two theoretical methods will be explored. We will adopt the quasichemical approximation (QCA) to the statistical mechanics of interstitial solutions.[13,24–28] In the QCA all interstitial sites are available for mixing, but the C atoms are regarded as exerting a repulsive force on each other, so that they enter adjacent interstitial positions less frequently than in a random distribution. Thus the QCA will allow us to treat soft-blocking effects in austenite. The key parameters in this treatment are the energies of formation of the C-C and C-V pairs, which will be accurately determined by analyzing a_c data.[19] These pair formation energies will be used to perform Monte Carlo (MC) simulations for various values of the ratio $y=N_C/N_{Fe}$. In this way, the average distribution of interstitials will be calculated as a function of composition. Further, the theoretical distribution of C atoms and V will be compared with the corresponding Mössbauer information.[29,30]

In spite of the fact that Mössbauer spectroscopy is one of the most sensitive methods to determine the local atomic

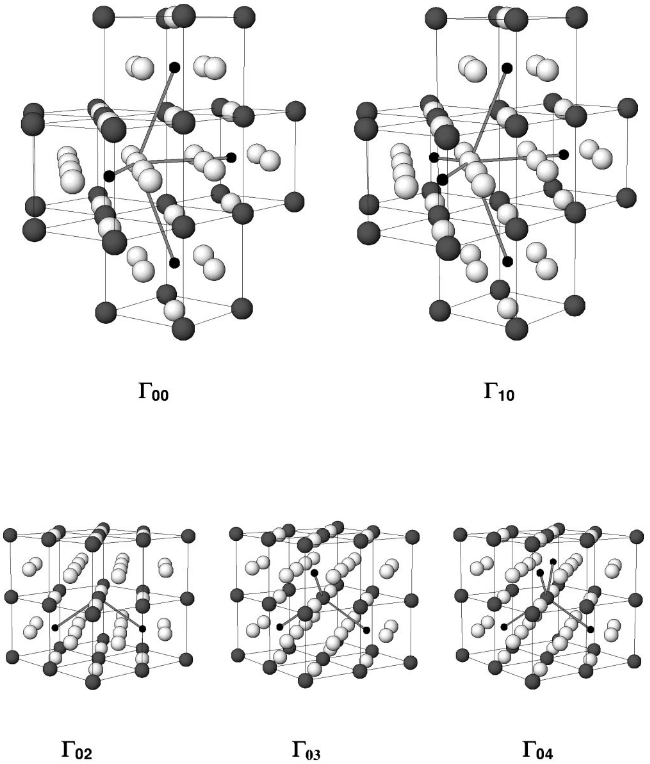

FIG. 1. Fe environments in the $Fe_8C_{(1-x)}$ model (Refs. 32 and 33). White and gray circles correspond to Fe atoms. Small black circles correspond to C atoms.

distribution around the Fe atoms, a controversy still exists concerning the detected Fe environments and their associated hyperfine interactions needed to analyze the austenite pattern.[31–35] In the analysis of the Mössbauer spectra various assumptions about the distribution of C in the octahedral interstitial sites have been proposed.[31–35] The first model was proposed by Genin and Flinn,[31] who detected only two different spectral components attributed to two environments for the Fe probes, viz., Fe atoms without C nearest-neighbor atoms and Fe atoms with one C nearest-neighbor atom. This model was suggested for dilute solutions in which the 12 NIS's of a C atom should be excluded. Afterward the model was improved by considering the second C interstitial shell.[33] In this modified version the C atoms occupy only the center of the cubes in a $Fe_8C_{(1-x)}$ structure, so that three possible environments for Fe atoms, associated to different hyperfine interactions may be distinguished (Fig. 1), as follows.

(a) Fe atoms without nearest-neighbor and next nearest-neighbor C atoms, associated with the singlet (Γ_{00}).

(b) Fe atoms with one nearest-neighbor C atom but without next-nearest C neighbors, related to the doublet (Γ_{10}).

(c) Fe atoms without nearest-neighbor C atoms but with n next-nearest-neighbor C atoms ($n=1-4$), ascribed to the singlet (Γ_{0n}).

Alternatively, a model has been proposed[34] in which all octahedral sites of the fcc structure are available for occupation and no assumptions are made whatsoever about the distribution of the C atoms in the second interstitial shell, as follows

TABLE I. Lattice parameter a, determined from the diffractograms using the Rietveld method (Ref. 36) and corresponding to samples $S1$, $S2$, $S3$, $S4$, and $S5$. The C content was determined using the empirical relation of Ref. 37.

Sample	a (A)	y
$S1$	3.610_1	0.052_1
$S2$	3.626_1	0.076_1
$S3$	3.628_1	0.079_1
$S4$	3.630_1	0.082_1
$S5$	3.632_1	0.086_1

(a) Fe atoms without nearest-neighbor C atoms, associated with the singlet (Γ_0).

(b) Fe atoms with one nearest-neighbor C atom, or Fe atoms with two nearest-neighbor C atoms at 90° from each other, related to the doublet (Γ_1).

(c) Fe atoms with two C atoms placed at opposite nearest sites (180°), ascribed to the doublet (Γ_2).

The purpose of the present paper is to provide information about the distribution of C atoms in the octahedral sites of the austenite phase by combining MC calculations, activity data,[19] and Mössbauer results.[29,30]

II. EXPERIMENT

Five samples with different C contents among those characterized in Refs. 29 and 30 were selected for the present study. In order to determine the C concentration, x-ray diffraction measurements were performed in a Phillips PW1710 diffractometer, using the monochromatic $K\alpha$ radiation of Cu, in Bragg Brentano's geometry, with a step mode collection of 0.02 and 10 s by step and with 2θ ranging from 39° to 98°. The x-ray patterns (not shown) were analyzed with the Rietveld method.[36] The actual C concentration in the samples was determined by combining the lattice parameters a extracted from the diffraction patterns with the known a versus composition relation for fcc Fe-C alloys.[37] The resulting lattice parameter and the inferred y values for the various alloys are listed in Table I.

The corresponding Mössbauer spectra, obtained as described in Refs. 29 and 30, are shown in Fig. 2. The central subspectra were associated with austenite, and the external lines on the spectra with ferrite/martensite phases.[37] The hyperfine parameters and the relative fractions associated to the various Fe environments according to the $Fe_8C_{(1-x)}$ (Refs. 32 and 33) and the random model[34] are listed in Table II. The contribution to the spectra of the doublet Γ_2 associated to Fe sites with two C atoms placed in opposite interstitial sites[34] resulted to be undetectable in our spectra.

III. THEORY

A. Monte Carlo simulations

The austenite interstitial solid solution is described as a lattice gas of N_C carbon atoms and N_V vacancies, distributed in the $N(=N_{Fe}=N_C+N_V)$ octahedral interstitial sites of the fcc structure, where N_{Fe} is the number of iron atoms. The

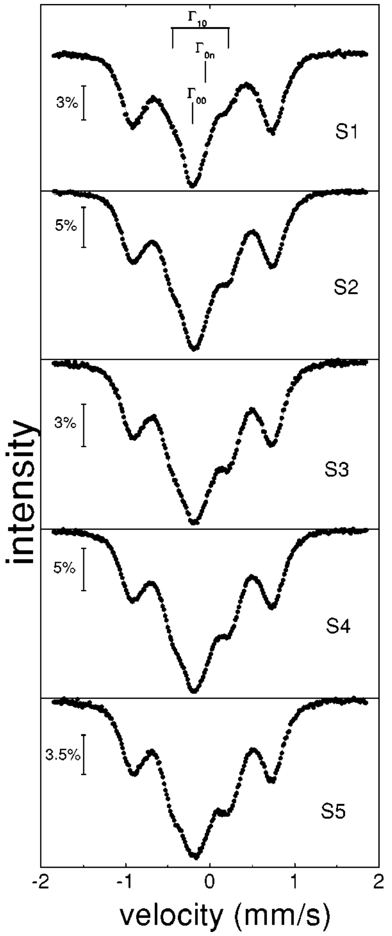

FIG. 2. Mössbauer spectra recorded for samples $S1$–$S5$. The bars on the top indicate the hyperfine interactions Γ_{10},Γ_{00}, and Γ_{0n}, associated win the $Fe_8C_{(1-x)}$ model (Refs. 32 and 33).

occupancy of the first and second interstitial shells was accounted for in three-dimensional MC simulations to calculate the number n_{ij} (i,j=C or V) of C-C, C-V, and V-V pairs, the relative fractions f_{pq} (p,q the numbers of C atoms in the first and second coordination shells, respectively) associated to the different Fe environments, and the number c_{i0} of C atoms having i C atoms in the first interstitial coordination shell and none in the next interstitial shell. The fraction f_0 involved in the random model[34] for Mössbauer spectra was calculated as $f_0 = f_{00} + \Sigma_{n=1}^{8} f_{0n}$.

A Fortran 77 routine using the Monte Carlo method, an Ising-type Hamiltonian, and periodic boundary conditions was developed. The Metropolis method was used to define the probability of the jump steps for C atoms. A randomly chosen C atom has the probability P to jump to an empty interstitial neighboring site, also randomly chosen, viz.,

$$P = \begin{cases} \exp[(\varepsilon_{Ti} - \varepsilon_{Tf})/RT] & \text{if } \varepsilon_{Tf} > \varepsilon_{Ti} \\ 1 & \text{if } \varepsilon_{Tf} \leq \varepsilon_{Ti} \end{cases}, \tag{1}$$

where ε_{Ti} and ε_{Tf}, are the initial and final total energies, respectively, calculated using the relation $\varepsilon_T = n_{C-C}\Delta\varepsilon$. Here $\Delta\varepsilon = \varepsilon_{C-C} - 2\varepsilon_{C-V}$ is the energy of formation of a C-C pair of nearest-neighbor C atoms relative to the individual C atoms (see Sec. III B), n_{C-C} is the number of C-C pairs, ε_{C-C} and ε_{C-V} are the interaction energies of the C-C and C-V pairs, respectively, R is the gas constant, and T is the temperature in K. If the atom movement decreases the total energy, the jump is allowed ($P=1$), but if the total energy increases the jump is allowed with a probability $P = \exp[(\varepsilon_{Ti} - \varepsilon_{Tf})/RT]$. The Fe atoms remain still during the simulation, and their positions were only used to calculate the number of n_{ij} pairs and the relative fractions f_{pq} associated with the different Fe environments.

To study the convergence of the results, cells of 4^3, 6^3, 8^3, and 10^3 were used. For simulations using cell sizes of 6^3 and higher the n_{ij} and f_{pq} fractions did not vary; hence cells of 864 Fe atoms and the corresponding number of C atoms were employed to decrease the calculation time. For all C concentrations, the equilibrium of the system was reached approximately at three MC steps, where a MC step is defined as N_C attempts to move a C atom. Finally, the occupation of the interstitial sites was characterized by using the average number z of empty NIS, which was calculated from the MC results as follows:

$$z = \frac{\sum_{i=0}^{12} c_{i0}(12-i)}{\sum_{i=0}^{12} c_{i0}}. \tag{2}$$

TABLE II. Hyperfine parameters and relative fractions f_{pq} of the different Fe environments found in austenite using the models of Refs. 32–34.

	$Fe_8C_{(1-x)}$model								Random model			
	Γ_{00}		Γ_{0n}			Γ_{10}			Γ_1		Γ_0	
Sample	δ mm/s	f_{00} %	δ mm/s	f_{0n} %	Δ mm/s	δ mm/s	f_{10} %	Δ mm/s	δ mm/s	f_1 %	δ mm/s	f_0 %
$S1$	-0.1	43_1	0.05_1	16_1	0.66_1	-0.01_1	41_2	0.61_1	-0.01_1	43_2	-0.07_1	57_1
$S2$	-0.1	33_1	0.05_1	23_1	0.67_1	0.01_1	44_2	0.62_1	0.01_1	48_1	-0.05_1	52_1
$S3$	-0.1	29_7	0.06_1	23_1	0.67_1	0.01_1	48_3	0.63_1	0.02_1	51_1	-0.04_1	49_1
$S4$	-0.1	27_1	0.06_1	21_1	0.67_1	0.01_1	52_2	0.63_1	0.02_1	50_1	-0.04_1	50_1
$S5$	-0.1	24_2	0.05_1	25_2	0.67_1	0.01_1	51_3	0.63_1	0.02_1	56_1	-0.03_1	44_1

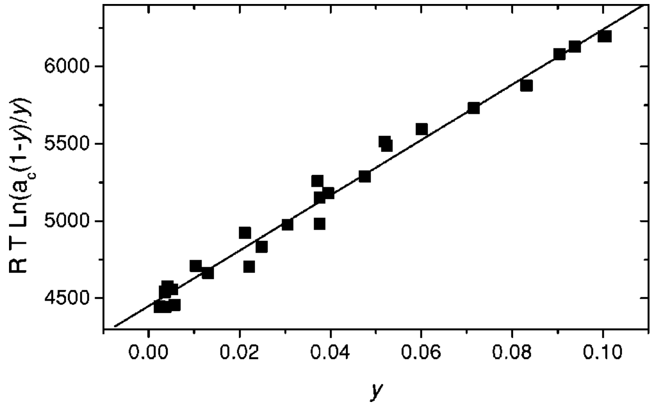

FIG. 3. Linear fit for activity data of Ref. 19. The values $\Delta\varepsilon = +1492_{39}$ cal mol^{-1} and $\Delta G_c = 4451_{25}$ cal mol^{-1} were determined.

B. Quasichemical model calculations

The energy of formation of a C-C pair that enters in the MC calculation was determined by analyzing experimental a_c data in terms of the QCA developed by Bhadeshia[27,28] for the Fe-C solutions. This formalism yields, for the activity a_c,

$$a_c = \frac{y}{1-y} \exp\left[\frac{\Delta G_c}{RT}\right] \times \left\{ \left(\frac{y}{1-y}\right)^2 \left(\frac{1-y-\frac{\overline{\lambda}}{N_V}}{1-y} \right) \right\}^{-Z/2} \exp\left[\frac{+Z\Delta\varepsilon}{2RT}\right], \qquad (3)$$

where $Z(=12)$ is the number of NIS's, and ΔG_c is the Gibbs energy of C in the standard state in austenite relative to graphite. The value of the parameter $\overline{\lambda}$ that minimize the Gibbs energy is

$$\overline{\lambda} = \frac{N_V}{2\sigma}\{1 - [1 - 4\sigma y(1-y)^{1/2}]\},$$

with

$$\sigma = 1 - \exp\left[\frac{-\Delta\varepsilon}{RT}\right].$$

A linear approximation of Eq. (3), appropriate for describing the dilute solution range, was fitted to carbon activity data measured at 1423 K.[19] A least-squares fit of the equation,

$$RT \ln\left[a_c \frac{1-y}{y}\right] = yZ\Delta\varepsilon + \Delta G_c ,$$

which is shown in Fig. 3 yielded $\Delta G_c = 4451_{25}$ cal mol^{-1} and $\Delta\varepsilon = +1492_{39}$ cal mol^{-1}. This $\Delta\varepsilon$ value was later used in the MC simulations.

The number of pairs n_{ij} calculated for $0 < y < 1$ using the quasichemical formalism (Table III) are plotted in Fig. 4 together with the n_{ij} determined using MC calculations. The inset gives a comparison for the composition range corresponding to the experimental solubility of C in austenite, viz., $y < 0.1$. There is a very good agreement between the QCA and MC predictions for n_{ij}, which encourages a discussion of the MC results for the relative fractions f_{pq} of the various Fe environments, as functions of y.

TABLE III. Pair interaction energies and number of n_{ij} pairs in the austenite phase obtained using the quasichemical model (Refs. 26–28).

Kind of pair	Number of pairs (n_{ij})	Energy per pair
V-V	$n_{V-V} = \frac{1}{2}$ Z N (1-y-λ)	0
C-V+V-C	n_{C-V}=Z N λ	ε_{C-V}
C-C	$n_{C-C} = \frac{1}{2}$ Z N (y-λ)	ε_{C-C}

IV. DISCUSSION

A. Monte Carlo simulation versus Mössbauer results

The f_{pq} vs y fractions obtained by MC calculations are plotted in Fig. 5. The environments of Fe atoms which contribute most are those without C atoms in the first interstitial shell, corresponding to fractions f_{00} and f_{0k}. Next in importance is the contribution f_{10} of environments with one C atom in the first interstitial shell and none in the second, whereas the relative fraction f_{pq} of Fe atoms having the first and second shells occupied varies between 8% and 15%. Finally, the relative fraction f_{20} of Fe atoms with more than one C atom in the first interstitial shell and without C atoms in the second shell is negligible, which reflects the repulsion between interstitial C atoms and suggests some blocking effect of the NIS in austenite. Two main consequences of the present f_{20} results may be highlighted. First, the Fe environments contributing to f_{pq} should be mainly f_{1k}. Second, Oda *et al.*[34] performed MC calculations which were interpreted

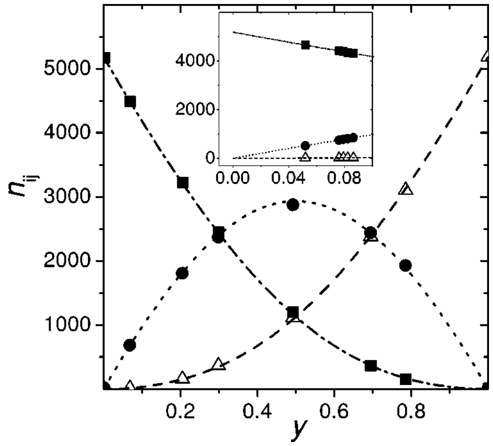

FIG. 4. The number n_{ij} (i,j=C or V) of pairs C-C, C-V, and V-V. Squares, triangles, and circles represent V-V, C-C, and C-V pairs respectively, obtained from Monte Carlo simulations using $\Delta\varepsilon = 1492$ cal mol^{-1}. (a) Dash-dotted line: V-V. (b) Dashed line: C-C pairs. (c) Dotted line: C-V pairs, calculated using the quasichemical model with the same $\Delta\varepsilon$ value. The inset gives a comparison for the composition range corresponding to the experimental solubility of C in austenite, viz. $y < 0.1$.

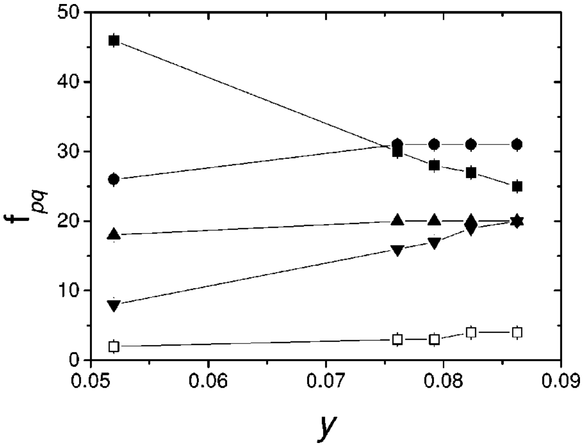

FIG. 5. The relative fractions f_{pq} (p,q is the number of C atoms in the first and second coordination shells, respectively) associated with the various Fe environments obtained using Monte Carlo simulations, as functions of C content. (a) Filled squares: f_{00}. (b) Filled circles: f_{0k}. (c) Up triangles: f_{10}. (d) Down triangles: f_{pq}. (e) Open squares: f_{20}.

by considering C atoms occupying the first interstitial shell either at 90° or at 180°. The present MC results, which account for the first and the second coordination shells, demonstrate that f_{20} is negligible and thus contradict the assumptions of their model.

We shall now discuss the comparison between the MC fractions (Fig. 5) with those extracted from Mössbauer spectra (Table II), viz., f_{00}, f_{10}, and f_{0n} using the Fe$_8$C$_{1-x}$ model[33] and f_0 and f_1 ($=1-f_0$) using the random model.[34] In Fig. 6 f_{00} and f_0 values obtained by MC simulations are compared with experimental results. According to Fig. 6 the random model underestimates the f_0 fractions significantly, whereas adopting the Fe$_8$C$_{(1-x)}$ model leads to a very good agreement between MC and Mössbauer results for f_{00}. It is tempting to take the results in Fig. 6 as further evidence in favor of the Fe$_8$C$_{(1-x)}$ model, which would not support the conclusions of Sozinov *et al.*[35] Their MC calculations were interpreted as indications that the Fe$_8$C$_{(1-x)}$ model is not adequate to represent the austenite phase. It is clear that the Fe$_8$C$_{(1-x)}$ model does not intend to treat explicitly the contribution of the Γ_{pq} configurations, which might very well be scattered at various positions of the spectra. Moreover, the Fe$_8$C$_{(1-x)}$ model involves the blocking of 12 sites around each interstitial atom; a complete discussion of its applicability to austenite should include a test of its predictions of the blocking effect. This issue will be dealt with in Sec. IV B.

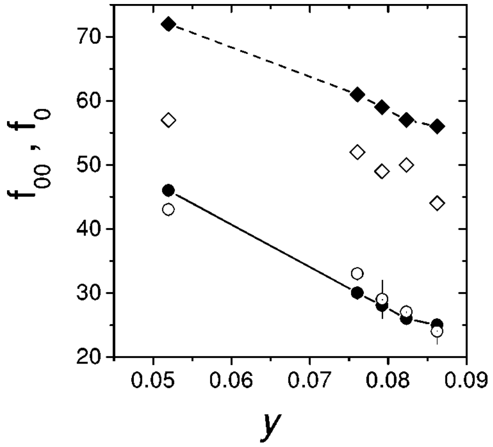

FIG. 6. The relative fractions f_{00} (circles) and f_0 (diamonds) associated with the various Fe environments obtained from Mössbauer data (open symbols) using the models (Refs. 33 and 34) referred to in Sec. I, compared with results from Monte Carlo simulations (filled symbols).

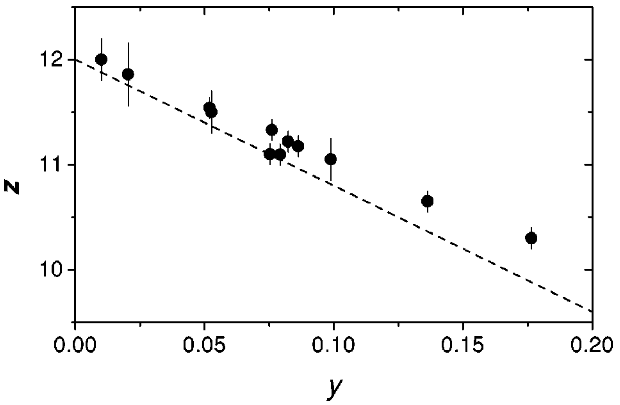

FIG. 7. The average number z of empty nearest neighbor interstitial sites of a C atom in austenite calculated as a function of composition using Monte Carlo simulations. (a) Filled circles: Monte Carlo simulations. (b) Dashed line: random mixture.

B. Account of blocking effects

In Fig. 7 the average number of empty NIS z obtained from the MC simulations is plotted as a function of y (symbols). The z values corresponding to the composition of the present experimental alloys are plotted using empty symbols. The dashed line in this graphic refers to the z value corresponding to a random mixture, viz., $z=12(1-y)$. The empty symbols in Fig. 7 indicate that already in alloys with $y=0.05$ the NIS's of the C atoms are, on the average, less occupied than in a random mixture. This fact is in qualitative agreement with the ideas behind the excluded-sites model, which motivates the following analysis of the blocking effects in models for a_c in austenite.

It was recently pointed out[23] that in a strict hard-blocking model, empty sites must be interpreted as blocked sites. This implies that the b parameter of the HBESM (Sec. I) should be considered as equal to z (Fig. 7). Two consequences of such interpretation will be discussed. The first consequence is that the MC results in Fig. 7 cannot be represented using the HBESM unless the b parameter is allowed to vary with composition. In qualitative agreement with this, Oates *et al.*[22] interpreted their own z values from MC calculations as a composition dependent b parameter, decreasing with the increase in the C content. However, the excluded-sites model does not explain the composition dependence of b, which has stimulated some attempts to improve the simple picture by invoking, e.g., an overlapping of the sites excluded by different interstitial atoms.[16,21–23] The second consequence of the current[23] interpretation of the hard-blocking is that Fig. 7

yields $b(=z)>10$ in the composition range $y<0.2$. However, these values cannot be reconciled with those extracted from experimental a_c data. The latter are integral and nonintegral b values falling in the range $3<b<5$.[9,19,21,23]

In view of these facts we conclude that the strict form of the excluded-sites model (Sec. I) does not seem able to account for the present blocking effects by using the same b values which are known to reproduce the experimental a_c data. It is also evident that a more realistic account of such effects would require abandoning the one-parameter formula for a_c, i.e., what has been considered as the main advantage of the HBESM.[23]

V. CONCLUSION

In the present study the energy parameters describing the interstitial solution of C in the fcc phase of Fe have been obtained by analyzing experimental thermodynamic data in terms of the quasichemical approximation, i.e., a Gibbs energy of C in austenite relative to graphite of $\Delta G_c = 4451_{25}$ cal mol^{-1} and a C-C pair formation energy of $\Delta\varepsilon = +1492_{39}$ cal mol^{-1} . These parameters have been used as input information in Monte Carlo simulations, and various key quantities have been obtained. In particular, the composition dependence of various f_{pq} ratios, describing the relative weight of the various Fe configurations contributing to the Mössbauer spectra of Fe-C austenite, have been predicted and compared with those derived by modeling the Mössbauer spectra. In this way, two alternative models[32–34] for the distribution of the C atoms in the interstitial sites have been tested. Monte Carlo results attest the C-C repulsion and show that there is a simultaneous occupation of the first and second interstitial shells. MC results also indicate that a description similar to the $Fe_8C_{(1-x)}$ structure[32,33] is somewhat more realistic than the random model[34] for the Fe-C austenite phase. Such a model[32,33] is usually associated to the blocking of some nearest interstitial sites by a C atom. Anyhow, three components Γ_{00}, Γ_{10}, and Γ_{0n} are the only components that can be detected by fitting the Mossbauer spectra. Other Fe environments, which are quantified by the MC simulation under the denomination Γ_{nm}, are clearly a minority, which does not exceed 15% as a whole and scattered at various spectral positions, hidden within the noise of the spectrum. Therefore, it is impossible to postulate that the number of blocked sites around a C interstitial is less than 12 from the sole Mössbauer measurements. The MC simulation gives this extra information explaining why it would be illusory to try to go further for fitting the Mössbauer spectra. The present results cannot be accounted for by the simplest hard-blocking excluded sites model, often used to provide a one-parameter formula for the activity of C in austenite.

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