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Cite as: AIP Advances 4, 017128 (2014); <https://doi.org/10.1063/1.4863462>

Submitted: 23 December 2013 • Accepted: 15 January 2014 • Published Online: 23 January 2014

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## Calculation of self-diffusion coefficients in iron

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(Received 23 December 2013; accepted 15 January 2014; published online 23 January 2014)

On the basis of available  $P$ - $V$ - $T$  equation of state of iron, the temperature and pressure dependence of self-diffusion coefficients in iron polymorphs ( $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\varepsilon$  phases) have been successfully reproduced in terms of the bulk elastic and expansivity data by means of a thermodynamical model that interconnects point defects parameters with bulk properties. The calculated diffusion parameters, such as self-diffusion coefficient, activation energy and activation volume over a broad temperature range (500–2500 K) and pressure range (0–100 GPa), compare favorably well with experimental or theoretical ones when the uncertainties are considered. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4863462>]

Iron is a very common metal for a wide range of practical applications. Under ambient conditions, Fe adopts a body-centred cubic ( $bcc$ ,  $\alpha$  phase) structure that transforms with temperature to a face-centred cubic ( $fcc$ ,  $\gamma$  phase) form<sup>1</sup> (at  $\sim 1200$  K),  $bcc$  ( $\delta$  phase) and liquid. While, at high pressure, the  $\alpha$  phase transforms to a hexagonal close-packed ( $hcp$ ,  $\varepsilon$  phase) structure<sup>2–5</sup> (at  $\sim 10$ – $15$  GPa), the phase diagram of Fe polymorphs has been shown in Fig. 1. The physical properties of iron and its alloys are of considerable interest to both material scientists and geophysicists. In particular, iron is considered as the major component of the Earth's core.<sup>6</sup> It is known that the diffusion is related strongly to the creep, grain boundary motion and solid phase transition in a metal and alloy. Therefore, a knowledge of the transport properties of iron and its alloys is important for understanding the evolution and current dynamics of the cores of many of the planets, including Earth.

The self-diffusion and impurity diffusion in pure iron have been studied extensively by experimental and theoretical investigations in the past decades. It is worth noting that, most of previous self-diffusion experiments were performed at ambient conditions (including  $\alpha$ ,<sup>7–10</sup>  $\delta$ <sup>11</sup> and  $\gamma$ <sup>12</sup> phases), while very few experimental measurements or theoretical calculations of self-diffusion in Fe polymorphs were reported simultaneously at high pressure and high temperature, especially for  $\gamma$  and  $\varepsilon$ -Fe. Thus, it is very difficult to extrapolate these atmospheric results to the deep planetary interiors. In the absence of direct experimental/or theoretical data, the existence of alternative approaches are also indispensable for predicting diffusion-related problems and thermodynamic properties at conditions of pressure and temperature, which are difficult to access by experimentation or where experimental data are lacking. Almost 60 years ago, a celebrated model<sup>13</sup> (termed as Zener model) was proposed to connect defect parameters with bulk macroscopic properties in which the Gibbs free energy  $g^{\text{act}}$  is proportional to the shear modulus  $\mu$  of the solid. However, a recent study<sup>14</sup> demonstrated that the predicted various defect processes (i.e., formation, migration and self-diffusion) by the Zener model deviated strongly from the experimental behavior in a large variety of solids (for more details see Ref. 14). In addition, to our knowledge, few data on the shear modulus of Fe polymorphs were experimentally reported simultaneously at high temperature

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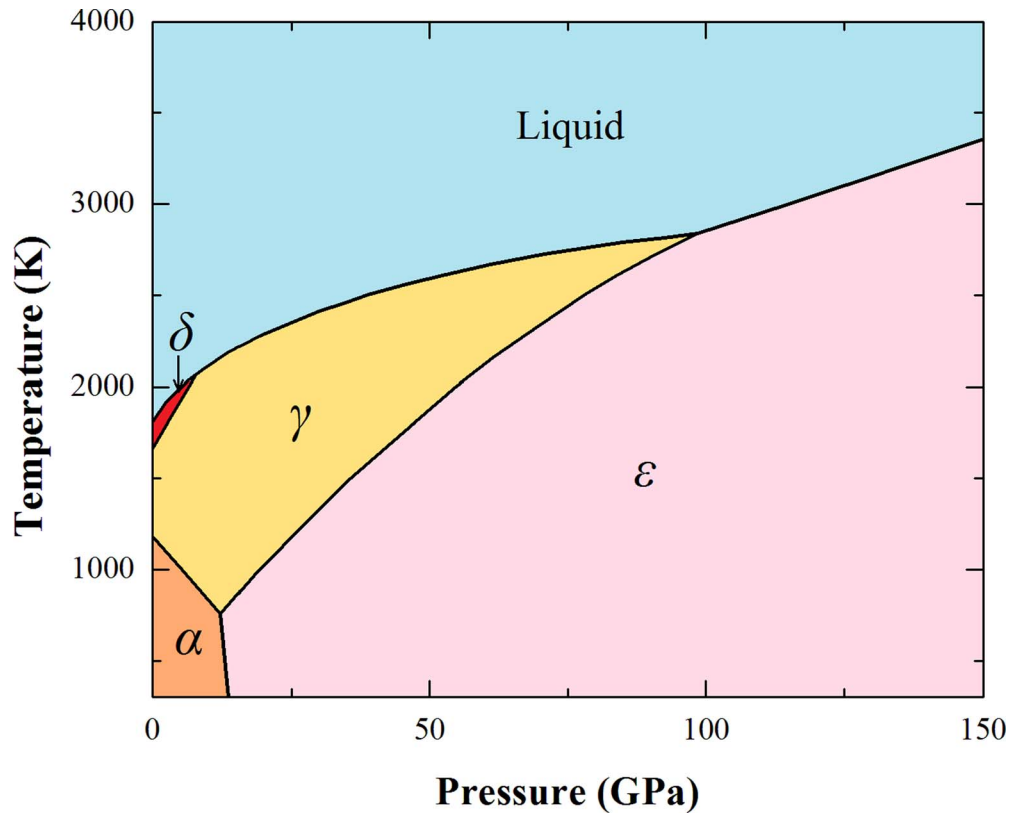


FIG. 1. Phase diagram of Fe. The phase boundary is based on previous experimental data.<sup>1-4</sup>

and high pressure. Consequently, these deficiencies prevent us from directly applying the Zener model to calculate the self-diffusion coefficients in Fe polymorphs as a function of pressure and temperature. On the other hand, about 30 years ago, Varotsos and Alexopoulos<sup>15,16</sup> proposed another thermodynamic model (the so-called cBΩ model) to calculate defect parameters in solids, in which the Gibbs free energy  $g^{\text{act}}$  should be proportional to the isothermal bulk modulus  $B$  and the mean volume  $\Omega$  per atom. It is worth noting that, this model has been successfully applied to a variety of cases including rare gas solids,<sup>15</sup> fluorides,<sup>17,18</sup> diamond<sup>19,20</sup> and viscous liquids.<sup>21</sup> Furthermore, its validity has been recently extended in self- or heterodiffusion in geomaterials.<sup>20,22-28</sup> Here, our goal is to examine whether the thermodynamic cBΩ model, together with the recent  $P$ - $V$ - $T$  equation of state of iron investigated by *in situ* X-ray diffraction<sup>1-5,29</sup> and theoretical calculations,<sup>30,31</sup> can be applied to estimate the self-diffusion coefficient in Fe polymorphs over wide ranges of  $P$  and  $T$ .

In all of the diffusivity calculations discussed in this paper we assume that diffusion is governed by a monovacancy mechanism mediated by nearest-neighbor vacancy hops. Under this assumption, the self-diffusion coefficient  $D$  for a single diffusion mechanism operating in monoatomic crystals, is described in terms of the activation Gibbs free energy  $g^{\text{act}}$ :<sup>15,32</sup>

$$D = f a^2 \nu \exp \left[ -g^{\text{act}} / (k_B T) \right] \quad (1)$$

where  $f$  is a correlation factor depending on the diffusion mechanism and structure,  $a$  is the jump distance that is actually equal to the lattice constant,  $\nu$  is the corresponding jump frequency which is the order of the Debye frequency  $\nu_D$ ,<sup>15</sup>  $k_B$  is Boltzmann constant,  $T$  is the absolute temperature.

The Gibbs free energy  $g^{\text{act}}$  for the activation process is interconnected with the bulk properties of solids according to the cBΩ thermodynamic model:<sup>14-16</sup>

$$g^{\text{act}} = c^{\text{act}} B \Omega \quad (2)$$

where  $B$  is the isothermal bulk modulus,  $\Omega$  is the mean atomic volume per atom, and  $c^{\text{act}}$  is a dimensionless factor that may be considered in a first approximation to be independent of temperature and pressure.

Since  $g^{\text{act}}$  is proportional to the quantity  $B\Omega$ , by inserting Eq. (2) into Eq. (1) we can write  $D$  in terms of the  $cB\Omega$  model:

$$D = f a^2 \nu \exp[-c^{\text{act}} B \Omega / (k_B T)] \quad (3)$$

If for a given temperature  $T_1$  the diffusion coefficient  $D_1$  is known, one can calculate the value of  $c^{\text{act}}$  from Eq. (3) by the following formula:

$$c^{\text{act}} = \frac{k_B T_1}{B_1 \Omega_1} \ln \frac{f a_1^2 \nu_1}{D_1} \quad (4)$$

where the subscript 1 stands for the value of the respective quantity measured ( $a_1$ ,  $\nu_1$ ,  $B_1$  and  $\Omega_1$ ) at  $T_1$ . Once the value of  $c^{\text{act}}$  has been determined through Eq. (4), Eq. (3) allows the estimation of the diffusion coefficient  $D$  at any  $T$  (or  $P$ ) provided that appropriate values of  $f$ ,  $a$ ,  $\nu$ ,  $B$  and  $\Omega$  are available at the corresponding temperature.

In order to determine the value of  $c^{\text{act}}$  more precisely, several novel methods have been employed to accomplish this, such as single experimental measurement,<sup>14–16,25,27,33,34</sup> compensation law<sup>23,24</sup> and “mean value method”.<sup>20,22,27,28</sup> On the other hand, several potential factors<sup>15,23,27,28</sup> could affect the degree of accuracy of the calculated value of  $c^{\text{act}}$ , including experimental uncertainties of diffusion coefficients, elastic parameters,  $\nu$ ,  $B$ ,  $\Omega$ , etc. Nevertheless, the resultant predicted diffusion diffusivities still remain within the experimental uncertainties.<sup>20,22,27,28</sup> In the present case, the mean value method has been applied to determine the constant  $c^{\text{act}}$  in Eq. (4).

Before starting to reproduce the self-diffusion coefficients in iron polymorphs by means of Eq. (3), the following two points have to be emphasized: (1) Experimental measurements<sup>7–10</sup> showed a *magnetic diffusion anomaly*, that the temperature dependence of the lattice self-diffusion coefficient largely deviated from the Arrhenius behaviour due to the magnetic order-disorder transition in  $\alpha$ -Fe through the Curie temperature ( $T_C = 1043$  K). Although an elastic anomaly<sup>35</sup> has been used to account for the nonlinear Arrhenius plots for self-diffusion in pure  $\alpha$ -Fe, however, such magnetic effect on the bulk properties (especially for the bulk modulus  $B$  and the volume thermal expansion coefficient  $\beta$ ) of  $\alpha$ -Fe has never been reported at high pressure and temperature so far. Thus self-diffusion coefficients in  $\alpha$ -Fe were separately reproduced in ferromagnetic ( $T < 1043$  K) and paramagnetic ( $1043 \text{ K} < T < 1184 \text{ K}$ ) phase. (2) To the best of our knowledge, there are no theoretically or experimentally reported self-diffusion coefficients available in pure  $\varepsilon$ -Fe (*hcp*) because of a critical challenge in accomplishing the extreme  $P$ - $T$  conditions of planetary interiors. Nonetheless, Brown and Ashby<sup>36</sup> showed that a wide variety of *hcp* and *fcc* metals have similar diffusivities at the same homologous temperatures. Subsequently, the most recent measurements<sup>37,38</sup> revealed that the difference in Fe-Ni diffusivity and Fe or Ni self-diffusion is indistinguishably small within uncertainty. Therefore, the experimental results of interdiffusion rates in Fe-Ni alloys (90% Fe) at 23 GPa<sup>37</sup> were used as reference data to examine the validity of the  $cB\Omega$  model for self-diffusion in  $\varepsilon$ -Fe in this work.

We can now refine the temperature dependence of the self-diffusion coefficient in Fe polymorphs ( $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\varepsilon$  phases). In order to do this, first of all, we have to calculate the value of  $c^{\text{act}}$  using Eq. (4). Here, for the sake of simplicity, the self-diffusion in  $\alpha$ -Fe were treated as an example to show how the diffusivities reproduced by the  $cB\Omega$  model. Below the Curie temperature, each experimental temperature is used to calculate the corresponding expansivity and elastic data ( $a$ ,  $B$ ,  $\Omega$ ) based on the  $P$ - $V$ - $T$  equation of state of  $\alpha$ -Fe<sup>30</sup> by employing the same procedures presented previous studies.<sup>20,22,23,28</sup> If inserting the appropriate parameters (i.e.,  $f (= 0.727$  for  $\alpha$ -Fe),  $a$ ,  $\nu$ ,  $B$ ,  $\Omega$ ) and experimentally available diffusion data<sup>7–10</sup> into Eq. (4) for each  $T$ , we get the mean value  $c_{\text{mean}}^{\text{act}} = 0.1932 (\pm 0.0066)$  in ferromagnetic phase. Likewise, the value of  $c_{\text{mean}}^{\text{act}}$  was calculated to be  $0.1737 (\pm 0.0033)$  in paramagnetic phase. Once the value of  $c^{\text{act}}$  is now known, we can calculate the  $D_{\text{calc}}$  from Eq. (3) using the approximate elastic and expansivity data for every expected  $T$ . In the same way, our calculations can also be carried out for self-diffusion in  $\delta$ ,  $\gamma$  and  $\varepsilon$ -Fe.

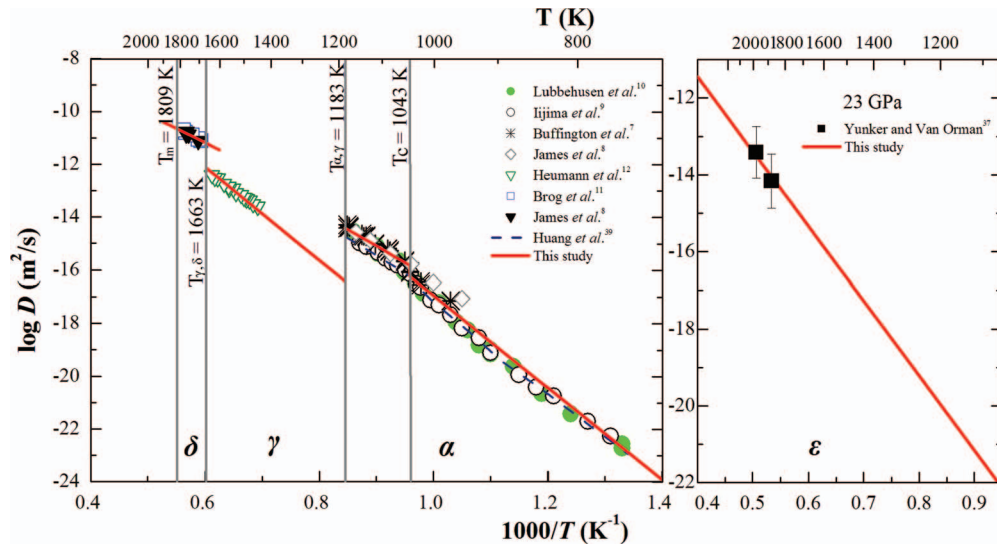


FIG. 2. Predicted temperature dependence of the calculated self-diffusion coefficients derived from the cBΩ model (red lines) vs. published experimental data in  $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\epsilon$ -Fe.

Fig. 2 compares the present predictions with the available experimental data for the temperature dependence of self-diffusion in iron. For self-diffusion in  $\alpha$ -Fe, the diffusivities are calculated from 500 to 1183 K, the  $\alpha \rightarrow \gamma$  transition temperature. The present calculations agree fairly well with the experimental<sup>7–10</sup>/or theoretical<sup>39</sup> determinations in the paramagnetic phase, while the calculated  $D_{\text{calc}}$  values overestimate slightly the measured values in the ferromagnetic phase at low temperature. It is noteworthy that, the present calculated  $D_{\text{calc}}$  in  $\alpha$ -Fe shows a slight jump across the Curie temperature ( $T_C = 1043$  K), this behavior differs considerably from those observed in experiment measurements<sup>7–10</sup> and theoretical calculation<sup>39</sup> where a continuous change is present at  $T_C$ . This discrepancy is mainly derived from two different  $c^{\text{act}}$  values are used in this calculation as aforementioned. On the other hand, the present calculations for  $D_{\text{calc}}$  derived from the cBΩ model match well the experimental results of  $\delta$ ,<sup>11</sup>  $\gamma$ <sup>12</sup> and  $\epsilon$ -Fe.<sup>37</sup> Obviously, these calculations suggest that the cBΩ model reasonably predicts the self-diffusivity within iron polymorphs.

Furthermore, pressure dependence of self-diffusion in Fe may be also investigated in the framework of the cBΩ model. From a thermodynamic point of view, if recalling the definition of activation volume  $v^{\text{act}} = -(\partial g^{\text{act}} / \partial P)_T$  and differentiating Eq. (1) with respect to pressure, we get the activation volume  $v^{\text{act}}(P, T) = -k_B T (\frac{\partial \ln D}{\partial P})_T$  for diffusion process (see page 126 of Varotsos and Alexopoulos).<sup>15</sup> Thus the quantity  $v^{\text{act}}$  can be estimated from the slope of the  $\ln D$  versus  $P$  plot (for additional details see Refs. 15, 20, 24, 27, and 28.). In addition, the following point should be emphasized. Since  $c^{\text{act}}$  is dimensionless factor which is considered to be independent of  $T$  and  $P$  to a first approximation,<sup>14–16,33</sup> in a similar manner, thus the calculation of pressure variation of  $D_{\text{calc}}$  at other temperatures can be performed through Eq. (3) by employing the same value of  $c^{\text{act}}$  as well as aforementioned temperature dependence of  $D_{\text{calc}}$ .

Fig. 3 presents a direct comparison between calculated and measured pressure-dependent diffusion coefficients for Fe self-diffusion. Remarkably, the calculated diffusivities  $D_{\text{calc}}$  derived from the cBΩ model are in good agreement with the experimentally reported  $D_{\text{exp}}$  for  $\alpha$ ,<sup>9,10</sup>  $\delta$ ,<sup>8,11</sup>  $\gamma$ <sup>7,12</sup> and  $\epsilon$ -Fe<sup>37</sup> (see Fig. 3(a)–3(d)). Further, an inspection of the calculated curve of Fig. 3 shows a linear behavior of  $\log D$  vs  $P$  plot corresponding to an activation volume independent of pressure for  $\alpha$ ,  $\delta$  and  $\gamma$ -Fe, but a slight upward curvature that implies a relatively large pressure dependence on the activation volume for  $\epsilon$ -Fe (Fig. 3(d)). The resultant diffusion parameters ( $D_0$ ,  $E$  and  $v^{\text{act}}$ ) for Fe polymorphs ( $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\epsilon$  phases) are listed in Table I. Clearly, the calculated activation energy and volume are comparable to the experimental or theoretical ones if the relevant uncertainties are taken into account. Especially, the present calculated  $v^{\text{act}}$  of 3.76–5.37 cm<sup>3</sup>/mol in  $\epsilon$ -Fe is in excellent



TABLE I. Comparison between calculated and experimental diffusion prefactor  $D_0$ , activation energy  $E$  and activation volume  $v^{act}$  for self-diffusion in  $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\varepsilon$ -Fe.

References	$v^{act}$	$T$ (K)	$P$ (GPa)	$D_0$ (m <sup>2</sup> /s)	$E$ (kJ/mol)	$v^{act}$ (cm <sup>3</sup> /mol)	Remarks
$\alpha$ -Fe							
Lubbehusen and Mehrer <sup>10</sup>		754.5–1032	1 atm	$6.8\text{--}27.7 \times 10^{-4}$	284.7–299.1		Ferromagnetic
		1054–1163	1 atm	$6.8\text{--}12.3 \times 10^{-4}$	248.0–258.6		Paramagnetic
James and Leak <sup>8</sup>		956–1040	1 atm	$2.75 \times 10^{-3}$	254		Ferromagnetic
		1081–1157	1 atm	$2.01 \times 10^{-4}$	240.6		Paramagnetic
Buffington <i>et al.</i> <sup>7</sup>		973–1043	1 atm	$2.0 \times 10^{-4}$	251		Ferromagnetic
		1053–1178	1 atm	$1.90 \times 10^{-4}$	239		Paramagnetic
Iijima <i>et al.</i> <sup>9</sup>		766–1042	1 atm	$2.76 \times 10^{-4}$	289.7		Ferromagnetic
		1052–1148	1 atm	$2.76 \times 10^{-4}$	250.6		Paramagnetic
Huang <i>et al.</i> <sup>39</sup>		0–1043	1 atm	$6.70 \times 10^{-5}$	277		Ferromagnetic
		1043–1184	1 atm	$6.70 \times 10^{-5}$	239		Paramagnetic
This study	0.1932	500–1184	0–20	$3.71 \times 10^{-4}$	269(5)	5.64–5.68	Ferromagnetic
This study	0.1737	500–1184	0–20	$9.97 \times 10^{-5}$	236(7)	5.22–5.26	Paramagnetic
$\delta$ -Fe							
Brog <i>et al.</i> <sup>11</sup>		1663–1783	1 atm	$1.90 \times 10^{-4}$	238(13)		
James and Leak <sup>8</sup>		1701–1765	1 atm	$2.01 \times 10^{-4}$	240(4)		
This study	0.1639	1500–2200	0–20	$1.29 \times 10^{-5}$	201 (6)	4.99 ~ 5.08	cB $\Omega$ model
$\gamma$ -Fe							
Heumann and Imm <sup>12</sup>		1443–1634	1 atm	$4.90 \times 10^{-5}$	284 (6)		
This study	0.1659	1000–2500	0–50	$2.77 \times 10^{-2}$	337(10)	4.17 ~ 4.97	cB $\Omega$ model
$\varepsilon$ -Fe							
Yunker and Van Orman <sup>37</sup>		1423–1973	0–23	$2.70 \times 10^{-4}$	300	3.1, 6 $\S$	EPMA
This study	0.1453	1000–2500	0–100	$2.15 \times 10^{-4}$	372	3.76 ~ 5.37	cB $\Omega$ model

Standard deviation is given in parenthesis; EPMA: electron microprobe analysis.

$\S$  Ref. 40;

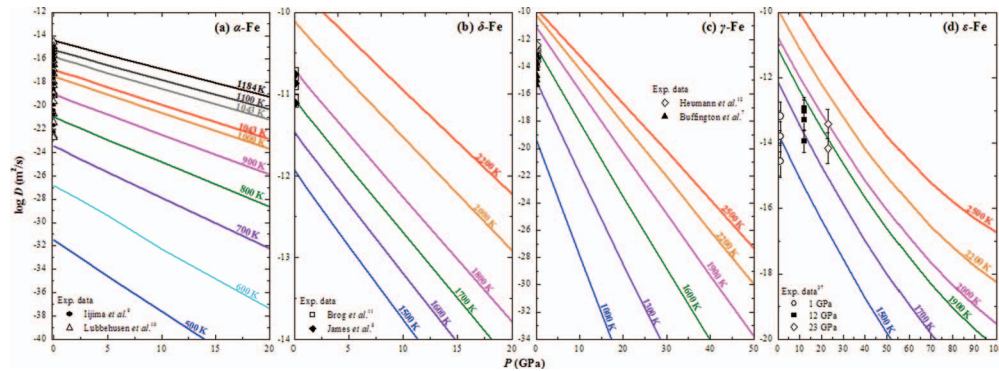


FIG. 3. Predicted pressure dependence of the calculated self-diffusion coefficients derived from the cB $\Omega$  model (solid lines) vs. published experimental data in (a)  $\alpha$ , (b)  $\delta$ , (c)  $\gamma$  and (d)  $\varepsilon$ -Fe.

agreement with the experimental one of 3.1–6 cm<sup>3</sup>/mol.<sup>37,40</sup> However, the thermodynamic estimates for  $v^{act}$  need to be further verified in the next future, because the experimentally or theoretically determined activation volumes of self-diffusion are not yet available for  $\alpha$ ,  $\delta$  and  $\gamma$ -Fe so far.

In summary, the validity of the thermodynamic cB $\Omega$  model is tested in terms of the experimentally determined self-diffusion coefficients in iron polymorphs ( $\alpha$ ,  $\delta$ ,  $\gamma$  and  $\varepsilon$  phases). An excellent agreement between the calculated self-diffusion coefficients ( $D_{calc}$ ) over a wide range of temperatures and pressures and the experimental data in each case, shows the credibility of describing Fe self-diffusion in terms of a thermodynamic model that interconnects the point defect parameters with bulk properties (i.e., the isothermal bulk modulus  $B$  and the atomic volume  $\Omega$ ). Particularly, the present approach has been satisfactory applied to the case of  $\varepsilon$ -Fe under the corresponding  $P$ - $T$  (up to

100 GPa and 2500 K) conditions of the lower mantle, such data should have important implications for the physical and chemical processes of deep planetary interiors.<sup>37,38</sup>

## ACKNOWLEDGMENTS

The authors acknowledge helpful and constructive comments from one anonymous reviewer and M. Paluch for his meticulous editorial handling of the work. This work was financially supported by National Natural Science Foundation of China (41303048) and partially supported by the Institute for Study of the Earth's Interior, Okayama University.

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