Bibliographical INDEX (1961 – 1998)

Pierre Vallet's and Associates' publications
about **non-stoichiometric iron** and **manganese monoxides**
or **wüstite** and **manganosite**

N°	Author(s)	Title	Reference
1	P.R.*, P.V.** *= **Paul Raccah**	Détermination de l'activité du fer dans la wüstite solide (Determination of the iron activity in solid wüstite)	***C.R.A.S.***[(a)] **253** **2682-84 (1961)**
2	P.R., P.V.	Sur quelques propriétés thermodynamiques de la wüstite, solution solide strictement régulière de fer et d'oxygène (On some thermodynamic properties of wüstite, a strictly regular solution of iron and oxygen)	***C.R.A.S.*** **254 1038-40 (1962)**
Thèse, Paul Raccah Ingénieur-Docteur		Etude des propriétés thermodynamiques du protoxyde de fer (Study of the thermodynamic properties of iron protoxide)	**Série B n°7, n°d'ordre 8 30/06/1962 Rennes- France**
3	P.R., P.V.	Sur l'application de la théorie de C. Wagner à la wüstite solide (On applying C. Wagner's theory to solid wüstite)	***C.R.A.S.*** **254 2555-57 (1962)**
4	P.R., P.V.	Nouveau réseau d'isothermes de la wüstite solide (New isothermal lines for solid wüstite)	***C.R.A.S.*** **255 1919-21 (1962)**
5	P.V., Maurice Kléman, P.R.	Sur de nouvelles propriétés thermodynamiques et un nouveau diagramme de la wüstite solide (On new thermodynamic properties and a new phase diagram of solid wüstite)	***C.R.A.S.*** **256 136-38 (1963)**
6	C. C.**, P.V.	Etude dilatométrique des diverses variétés de wüstite solide et existence d'un point triple métastable entre les trois variétés (Dilatometric study of wüstite subphases. Metastable invariant point for the three varieties)	***C.R.A.S.*** **Chimie physique 258 3281-84 (1964)**
7	P.V., P.R.	Sur les limites du domaine de la wüstite solide et le diagramme général qui en résulte (On the boundaries of the solid wüstite domain. General diagram)	***C.R.A.S.* Chimie physique 258 3679-82 (1964)**

http://gallica.bnf.fr/ark:/12148/bpt6k4011c.image.r=comptes+rendus+academie+sciences+paris+1963.f1301.langFR.pagination

N°	Author(s)	Title	Reference
8	P.V., C.C., P.R.	Valeurs des grandeurs thermodynamiques de la wüstite et de la magnétite solides (Thermodynamic properties of solid wüstite and magnetite)	***C.R.A.S.* Chimie physique 258 4028-31 (1964)**
9	C.C, D.W., P.V.	Variations du paramètre cristallin des trois variétés de wüstite solide dans leurs domaines d'existence respectifs (Variations of the cell parameter for the three wüstite subphases in their own stability domain)	***C.R.A.S.* Physique des solides 260 4325-28 (1965)**
10	P.V.	Sur de nouvelles frontières du domaine de la wüstite solide et les trois points triples qui en résultent à 910℃ (About new boundaries of solid wüstite domain and the three resulting triple points at 910℃)	***C.R.A.S.* Chimie physique 261 4396-99 (1965)**

P.V. = Pierre Vallet (1906-1994), D.W.** = Dominique Weigel, C.C.** = Claude Carel**
[(a)] = ***C****omptes* **R***endus Hebdomadaires de l'***A***cadémie des* **S***ciences de* **P***aris*

11 P.V., P.R. **Contribution à l'étude des propriétés thermodynamiques du protoxyde de fer solide** [ou *wüstite*]

(Contribution to the Study of the Thermodynamic Properties of Solid Iron Protoxide)

Mém. Sci. REV. MÉTALLURG. LXII n°1, 1- 29 (1965)

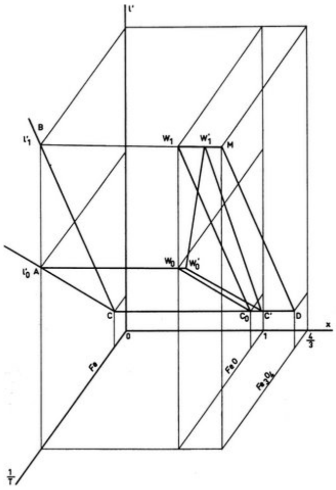


Fig.2 Schematic 3D diagram (1/T, *x*, *l'*) of solid W
Diagrams $W_0C_0W_1$↔stoichiometric FeO and W_0'C'W_1'↔ actual FeO*x*

Table I p.9: 185 associated values of *x* and *l'* (= $\log_{10}p_{O2}$, atm) at 21 temperatures Θ℃ ∈[800-1250].
The equilibrium oxygen pressure p_{O2} is generated by CO/CO2 mixtures. The solid composition parameter is *x* in actual FeO_x ($x\in$[1.042-1.20]).
Fig.5 - Set of isothermal lines *l'*(*x*) at Θ℃ ∈[920-1250], straight lines regression by the least squares method.
Fig.8 - Isothermal lines at Θ℃ ∈[800-900]. The line at 800℃ is curved. From 820 to 900℃, the isothermal lines are composed of two straight segments.
Figs.6 & 7- Variations of slope M(T^{-1}) and zero point ordinate N(T^{-1}) in relation *l'*= M*x* + N
Table III p.11: smoothed values of M and N, Θ℃ ∈[920-1250].
Tables V & VI p.14 & 15: M and N for lower and upper *x*, Θ℃ ∈[820-900].
Above 920℃, M and N can be developed as followi ng:
$M_i = a_i T^{-1} + b_i$ [11], $N_i = c_i T^{-1} + d_i$ [12], i =1,2,3;
Table IV p.13: coefficients a_i ,b_i ,c_i , d_i
Tables VII & IX p.16 & 19: measurements of equilibrium oxygen pressure on external boundaries Fe/W and W/Fe_3O_4 in columns "*Nos* mesures", 18 values (*l'₀*) and 10 values (*l'₁*) respectively.

See paper n °**7** phases and subphases (later said pseudophases) in W diagram, **first version** without separating W and W' at 911°C (αFe ↔γFe) : Pierre Vallet & Paul Raccah, Compt Rend Acad Sci Paris **258** 3679 (1964): **http://gallica.bnf.fr/ark:/12148/bpt6k4011c.image.r=comptes+rendus+academie+sciences+paris+1963.f1301.langFR.pagination**
See also **paper n° 27** [Contribution to the study of the non-stoichiometric iron monoxide. T-P-X diagram] P Vallet and C Carel, Mat. Res. Bull 14 1181 (1979) doi:10.1016/0025-5408(79)90213-7 , + some comments on the possible separation at 911°C in the case of second order transitions and only single subphase regions. See also papers n^{os} **43, 51**.

Thèse, Claude Carel Docteur ès Sciences Physiques	Recherches expérimentales et théoriques sur le dia-gramme d'état de la wüstite solide (Experimental and theoretical study of the state diagram of solid wüstite)	**Série B n°27 n° d'ordre 58, 7/07/1966 Rennes- France**

12 C.C. Sur la cinétique de réduction de la wüstite solide à l'intérieur des frontières de son domaine propre (Reduction kinetics of solid wüstite in its stability domain)

***C.R.A.S.* C265 533-36 (1967)**

Abridged english version:

Caption of the **Figure**: mean curves of the kinetics of mass variation as a function of time in coordinates [-log (ΔM/ΔM_0), log t]

Title of **Table I**: numerical values of n (equation (2): least squares regressions)

A. **Distinct reduction rates**. Runs of reduction above 910℃ by means of H_2/H_2O gas mixtures are available in ref.[1].
A numerical analysis was performed on the assumption of a kinetics expressed by a simple relation $\Delta M/\Delta M_0 = k.t^n$ (1)
By means of a logarithm transformation $\log (\Delta M/\Delta M_0) = n \log t + \log k$ (2)
the rate exponent n ~ (1.0, 0.75, 0.45, 0.25) is calculated for **I to IV** successive linear reduction patterns of each run (Table I).

1°) Runs recorded at 950 and 1000℃ are close one t o the other and remote from that at 1050℃. The horizontal stratification of Raccah's isothermal lines could be a factor justifying this gap.
2°) At the observed transitions **II→III**, **III→IV** and **II→IV**, a brief anharmonic phenomenon results in a short curved segment in the graph
3°) Such a segment is replaced by a discontinuity f or transition **I→II**
4°) Coefficients n ~0.75 (**II**) and ~0.45 (**III**) increase with increasing temperature

B. **Interpretation**. A mean coefficient of diffusion D (surface and mass phenomena) can be assessed following equation $1 - (\Delta M/\Delta M_0) = (8/\pi^2)\exp(-\pi^2 Dt / L^2)$ (3). Activation energies are E_{II} = 43.7 kcal/mole, E_{III} = 30.5 kcal/mole. E_{III} is in accordance with that in the literature [ref 7, 1965].

C. **Conclusion**. The reduction kinetics of Fe_3O_4 to wüstite in H_2/H_2O mixtures is linear as showed in [ref.5,1961] similarly to the rate of patterns **I**. It could indicate that some magnetite was formed in the sample when maintaining temporarily in static atmosphere. Are the three W_i -their different defect structures? - previously predicted [see paper n°7, 1964] underlying the kinetics patterns **II, III, IV** presently evidenced?
Ref. [1]: PFJ Landler & KL Komarek, Trans Met Soc A.I.M.E. 236 138-148 (1966)

13	Jean-Pierre Bars, C.C.	Etude dilatométrique de la wüstite solide à l'intérieur de son domaine d'existence (Dilatometric study of solid wüstite in its stability domain)	***C.R.A.S.*** **C269 1152-54 (1969)**
14	P.V., C.C.	Présentation du diagramme d'état du monoxyde de fer non-stoechiométrique : frontières du domaine et existence des trois variétés allotropiques (Non-stoichiometric iron monoxide: boundaries and existence of the three allotropic varieties)	***Ann. Chim.*** **5 n°4 246 - 49 (1970)** Colloq Internat **Oxydes ferreux et ses solutions solides**, ENSCParis **26-28 Mars 1969**
Thèse	**Jean-Yves BOUDONNET Doctorat de 3ème cycle**	Contribution à l'étude des propriétés thermomagnétiques de la wüstite solide entre 910 et 1100°C (Contribution to the study of the thermomagnetic properties of solid wüstite between 910 and 1100°C)	**Série B n°d'ordre 164, n°de série 108 27/ 11/ 1970 Rennes-France**
15	C.C.	Nouvelles mesures effectuées à haute température et équation de la frontière du domaine de la wüstite avec celui de la magnétite (Recent measurements at high temperature and equation of the boundary between wüstite and magnetite domains)	***C.R.A.S.*** **C273 393-95 (1971)**

thermogravimétrie, étude critique et théorique par **Pierre VALLET**
(thermogravimetry, critical and theoretical study)

Collection MONOGRAPHIES DE CHIMIE MINERALE, **Gauthier-Villars 1972**, pp. 388
[Index bibliographique : 503 références, table des auteurs cités (authors), Index des sujets traités (topics) liste des corps cités (addressed substances), Index des symboles algébriques (algebraic symbols)]

16	C.C., J.-Y. Boudonnet	Contribution à l'étude des propriétés thermomagnétiques de la wüstite solide au-dessus de 910°C (Contribution to the study of the thermomagnetic properties of solid wüstite above 910°C)	**Mém. Sci. REV. MÉTALLURG. LXX 3 179-86 (1973)**
17	C.C.	Sur une interprétation possible de mesures du paramètre cristallin de la wüstite solide en équilibre à 950 et 1050°C (About a likely interpretation of the cell parameter of solid wüstite under equilibrium at 950 and 1050°C)	***C.R.A.S.*** **C277 69-72 (1973)**
18	C.C.	Discussion de quelques résultats cristallographiques obtenus à l'équilibre thermodynamique sur la wüstite solide (Discussion about some crystallographic measurements in solid wüstite under thermodynamic equilibrium)	***C.R.A.S.*** **B278 417-20 (1974)**

19 P.V. Sur les propriétés thermodynamiques de la wüstite solide au-dessous de 911°C (About the thermodyna mic properties of solid wüstite below 911°C) ***C.R.A.S.*** **C280 239-41 (1975)**

Abstract - The properties of solid wüstite are different on both sides of 911°C. Presently a way to calculate these properties is proposed. Three varieties (*subphases, pseudophases*) W'1, W'2, W'3 are characterized numerically. That leads to calculate the phase boundaries: 1° α-iron/W'1, 2° magnetite/ W' 3, 3° W' 1/ W'2, 4° W' 2/ W'3, 5° W' 1/ W'3 (this latter is metastable)

20 P.V. Sur les propriétés thermodynamiques de la wüstite solide au-dessus de 911°C (About the thermodyna mic properties of solid wüstite above 911°C) ***C.R.A.S.*** **C281 291-94 (1975)**

Abstract - The four coefficients characterizing each of the three wüstite varieties W1, W2, W3 (*subphases, pseudophases*) are determined numerically from Raccah's isotherms (*wüstite under equilibrium*) following,a new method. The resulting equations are compared with those of Darken & Gurry's experimental isotherms at 1100, 1200, 1300°C, 1400°C (*quenched wüstite*), J.F. Marucco's isotherm at 1075°C, and B. Touzel in's isotherms at 1000 and 1075°C (*under equilibrium*)

21 C.C., J.-R.G.** Introduction to Description of Phase Diagram of Solid Wüstite: I. Structural Evidence of Allotropic Varieties (Introduction à la description du diagramme d'état de la wüstite solide : I preuves cristallographiques de variétés allotropiques) ***Mat. Res. Bull.*** **11 745-756 (1976)**

J.-R.G**= **Jean-Raymond Gavarri**

doi:10.1016/0025-5408(76)90154-9

22 J.-R.G., D.W., C.C. Introduction to Description of Phase Diagram of Solid Wüstite: II. Structural Review (Introduc tion à la description du diagramme d'état de la wüstite solide : II revue bibliographique structurale) ***ibidem*** **11 917-25 (1976)**

doi:10.1016/0025-5408(76)90164-1

23 J.-R.G., Carmen Berthet, D.W. Evolution structurale de la wüstite solide : variation du facteur d'agitation thermique isotrope moyen avec la température et la composition d'équilibre (Structural evolution of solid wüstite : variations of the mean isotropic factor with temperature and equilibrium composition) ***C.R.A.S.*** **C284 335-37 (1977)**

24 P.V. Sur les grandeurs thermodynamiques de la wüstite solide (About the thermodynamic properties of solid wüstite) ***C.R.A.S.*** **C284 545-48 (1977)**

25 J.-R.G., Carmen Berthet, C.C., D.W. Etude diffractométrique de l'ordre des lacunes et des ions interstitiels dans la wüstite solide de haute température (Diffraction study of the order of vacancies and interstitial ions in solid wüstite at high temperature) ***C.R.A.S.*** **C285 237-40 (1977)**

26 J.-R.G., C.C., D.W. Contribution à l'étude structurale de la wüstite solide de haute température (Contribution to the structural study of solid wüstite at high temperature) ***J. Sol. State Chem.*** **29 81-95 (1979)**

27 P.V., C.C. **Contribution à l'étude du monoxyde de fer solide non-stœchiométrique** [ou *wüstite*]**. Diagramme T-P-X (Contribution to the study of solid nonstoichiometric iron monoxide** [or wüstite]**. Diagram T-P-X) :** ***Mat. Res. Bull.*** **14 1181-1194 (1979**

DOI:10.1016/0025-5408(79)90213-7

Outline

Same notations as in paper n°11: FeO $_x$, l'= $\log_{10} p_{O2}$ (CO/CO2, 1 atm). The wüstite is a non-stoichiometric iron deficiency oxide $Fe_{1-z}O$ ($z \in$[0.05-0.17]). Parameter $x \in$ [1.05-1.21] is used preferentially in order to relate thermodynamically oxygen solid composition and equilibrium oxygen pressure.

The coefficients of equation of type **[1]** $l' = (a_i x + c_i)T^{-1} + b_i x + d_i$ are listed numerically in **TABLE 1** p.1186 (see identically in TABLE IV of paper n°11) . They correspond to three subphases W_i (i =1,2,3) between 920 and 1250°C and W'_i (i =1,2,3) between 900 and 800°C, (first approxim ation: **2nd method => Fig 3b**, p.1190).

Equation of type **[2]** $l' = (a_i x^2 + c_i x + e_i)T^{-1} + b_i x^2 + d_i x + f_i$ corresponds to an attempt to better fitting the apparently erratic variations of coefficients M & N of isotherms *l'(x)* (in Fig. 6 &7 p.12 &13 of paper n°11) ⇒ three subphases W'_i (so-called **3rd method**: the segments on the isotherms *l'*(*x*) are firstly distributed into three groups). The18 coefficients a_i to f_i (i =1,2,3) are listed in **TABLE 2** p.1187 **(=> Fig.5**, p.1191 **)**. The adjustment of the external boundaries is improved without being the last one (see paper n° **43**). The stable and metastable invariant points are listed, even those **(*)** not following the validity conditions at 911°C.

Two invariant points missing in 1979 are added presently (see also paper n°51), **X**: T = 1086 K, *x* = 1.0857, *l'* = -17.984 **Y**: T = 1068 K, *x* = 1.0857, *l'* = -18.424. They are the tips of a short vertical segment of boundary W'_1/W'_3. Its line suppressed a so-called *"grave anomalie"* indicated p.1192.

In Figs. below, the internal boundaries W'_1/W'_2 & W'_2/W'_3 are a*lmost* the continuation of boundaries W_1/W_2 & W_2/W_3 with an angular quasi-junction for the latter at 911°C. For their location in W' area, they look clos ely like the *extrapolated* dotted limits in Fig.2 p.795 from *Thermodynamic Properties of Fe1-xO. Transitions in the Single Phase Region*, B.E.F. Fender and F.D. Riley, J. Phys. Chem. Solids, 30, 793-798, (1969). Nevertheless, points R & R' or Q & Q' cannot be strictly superimposed, else 4 solid phases would be present at the sole invariant point **(*)**. The variance would be then equal to -1 (*The Fe-O System*, p.177, H.A. Wriedt, J. of Phase Equilibria <u>12</u> N°2 169-200 (1991)).

Anomalies remain at the temperature of the αFe↔γFe transformation. The molar properties $S_i°$ and $H_i°$ show weak discontinuities when crossing the line at 911°C at constant composition (see paper n° **43** 2ème partie, Table VIII p.728, and Figs 5 & 6 p.716 & 718) while heat content $C°_P(i)$ shows a jump (1ère partie, relation (49) ⇒ 2ème partie, Table VIII). No experimental information is available between 900 and 920°C to confirm p oints B to D, and the right ordering of chemical potentials of the three solid phases at each of these points.

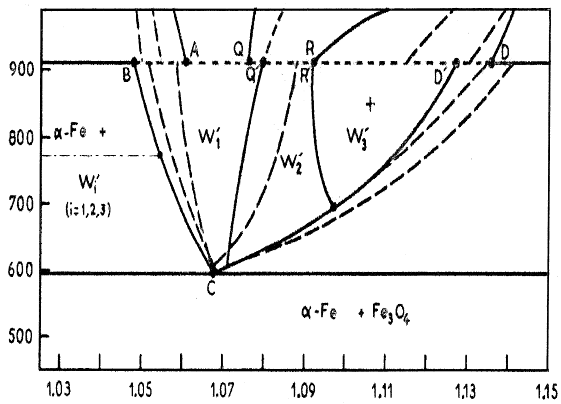


Fig.3b p.1190: equilibrium diagram of W' first approximation, equation of type **[1],**

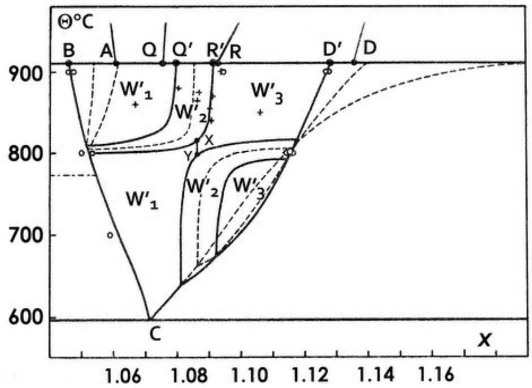


Fig.5 p.1191: following equation of type **[2]** better numerical fitting of lines *l'*(*x*), 3rd method

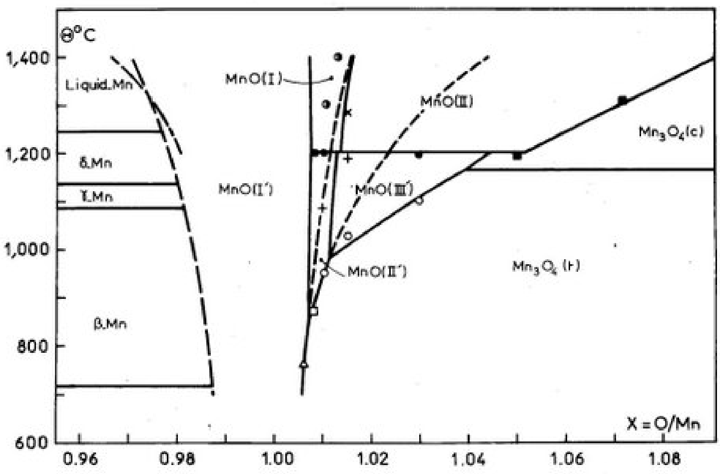
(*) In conformity with phase rule, double subphases domains between single subphase domains were proposed in terms of phenomenological description of binary diagrams in temperature range [900-920]°C.That would induce numerous eutectoid and peritectoid points at temperatures oscillating around 911°C (private communication at Un iversity of *Toulon et du Var*, A. Sebaoun, 04/24/1989). Prior to W and W' being separated, double subphases domains (with narrow Δ*x*) were also envisaged by modeling considerations in *Propriétés thermodynamiques du protoxyde de fer solide. Application de résultats expérimentaux au tracé du diagramme d'équilibre*, M. Kleman, Rev. Métall. Mém. Sci. <u>62</u> n°6, 457-69 (1965)

28 J.-R.G., C.C.	Evolution structurale de monoxydes non-stoechiomé-triques du type wüstite: Simulations et relations entre paramètres structuraux (Structure evolution in monoxides with wüstite type. Relations between structural parameters)	***J. Sol. State Chem.*** **<u>38</u> 368-80 (1981)**
29 J.-R.G., C.C., St.J.*, J.J.+ ***= Stanisława Jasienska** **+= Jan Janowski**	Morphologie et structures de la wüstite. Evolution des amas complexes et de l'ordre (Morphology and structure of wüstite. Evolution of defect clusters and the ordering)	***Rev. Chim. miné.*** **<u>18</u> n°6 608- 624 (1981)**
30 A.N.M.*, C.C. A.N.M.*= **Aron Naumovitch Men**	Investigation de la wüstite dans son domaine d'homo-généité par la méthode de composition des amas (Investigation of wüstite in its homogeneity range by means of the cluster component method - МКК) http://gallica.bnf.fr/ark:/12148/bpt6k56537784.image.f259.pagination	***C.R.A.S.*** **<u>294</u> II 253-56 (1982)**

31 C.C. Sur un tracé probable du diagramme d'état du monoxyde de manganese [ou *manganosite*]. (About a likely sketch of the manganese monoxide [or *manganosite*] state diagram) ***C.R.A.S.*** **<u>295</u> II 853-56 (1982)**

32 C.C. On a new T-P-X- Diagram of Manganese Monoxide [or *manganosite*] ***Proceed. 9th I.S.R.S. Sept.1-6, 1980, Crakow-Poland,*** **Materials Science Monographs, 10 Reactivity of Solids Vol 2 596-602 Elsevier PWN (1982)**

33 C.C. A Comparative Presentation of the Phase Diagrams of Iron and Manganese Monoxides. Structural Survey ***Proceed. First Round Table Meeting on Transport Structure and Phase Transformations in Iron and Manganese Oxides. Kozubnik-Poland Sept 8-9, 1980*** ***Bull. Acad. Min. Métall. Akademia Gorniczo Hutnicza, Im. St. Staszica w Krakowie*** **7- 20 1982R**



34 A.N.M., C.C. The Cluster Component Method (C.C.M.) in the Chemistry of Non-ideal Crystal Structures. Application to Wüstite (La méthode de composition des amas en chimie des structures cristallines non-idéales) Application à la wüstite. ***Solid State Chem. 1982 Proceed. 2nd Europ. Conf. June 7-9, 1982 Veldhoven-The Netherlands*** ***Studies in Inorganic Chemistry*** **Vol. 3 335-338 Elsevier (1983)**

35 J.-R.G., J.A.* *= **Jacek Arabski** Non-stoechiométrie et propriétés comparées des monoxydes de manganèse et de fer (Nonstoichiometry and compared properties of manganese and iron monoxides) ***C.R.A.S.*** **<u>296</u> II 949-52 (1983)**

36 A.N.M., C.C. Metod Klasternich Komponentov i Problema Trech Vioustitov (Katchestvenni Analiz) (Méthode de Composition des Amas et le problème des trois wüstites. Analyse qualitative) ***Doklady Akademii Nauk SSSR (Chimie Physique)*** **<u>270</u> N°2 374-75 (1983)**

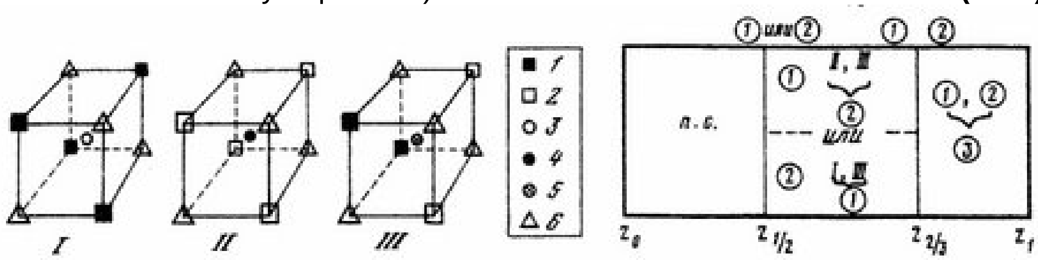


Рис. 1. Простейшие структуры г.ц.к. решетки вюстита и шпинели. Позиции: 16*d* (*1*), 16*c* (*2*), 8*b* (*3*); 8*a* (*4*), 48*f* (*5*), 32*e* (*6*) (см. табл. 7.1 [5])

Ref. [5]: A.N. Men, M.P. Bogdanovitch, Yu.P. Vorobiev, R.Yu. Dobrovinskii, V.M. Kamichov, V.B. Fetisov, Sostav-Defectnost-Svoistvo Tverdich Faz, Metod Klasternich Komponentov, Izdiatielsvo « Nauka », Moskow, 1977, p.186

See papers n°s 30, 34, 37, 41, 42

37 A.N.M., C.C. — Ordering in Wüstite and Manganosite (L'ordre dans la wüstite et la manganosite) ***Proceed. 2nd Round Table Meeting on Physico-Chemical Properties of Wüstite and Manganosite*, Sept 14-20 1983, Krakow-Krynica-Poland** — ***Bull. Acad. Min. Métall. Wydawnictwo AGH Krakow*** **49-66 (1985*)***

38 C.C., J.A., J.-R.G., St. J., J.J. — Thermodynamic Properties, Magnetic Transition, Transport Phenomena during Quenching, Brittleness and Morphology of Manganosite (Propriétés, transition magnétique, phénomènes de transport lors de la trempe, fragilité et morphologie de la manganosite) — ***ibidem*** **67-79 (1985)**

39 J.-R.G., J.A., St.J., J.J., C.C. — Structural Evolution of Manganosite : Comparison of Properties of Nonstoichiometric Manganese and Iron Monoxides (Evolution structurale de la manganosite : propriétés comparées des monoxydes non-stœchiométriques de manganèse et de fer) — ***J. Sol. State Chem.*** **58 56-70 (1985)**

40 J.-R.G., C.C., J.A. — La magnésiowüstite. Evolution structurale et déformation plastique (Magnesiowüstite. Structural evolution and plastic deformation) ***Proceed. 10th I.S.R.S. Dijon-France, August 27-31, 1984*** — ***Mater. Sci. Monographs*** **28 B, Reactivity of Solids *Part B* 763-66 Elsevier (1985)**

41 A.N.M., C.C., M.T. Varschavskii — Outchet Ouporiadotcheniia v Metode Klasternich Komponentov. Problema Trech Vioustitov (Modeling of the Ordering by Means of the Cluster Component Method. Problem of the Three Wustites) — ***Zhur. Fiz. Khim.*** **LIX N°6 1531-33 (1985)**

42 A.N.M., C.C. — The Cluster Component Method and Ordering in Nonstoichiometric Monoxides with the Rocksalt Structure (La Méthode de Composition des Amas et l'ordre dans les monoxydes non-stœchiométriques de structure NaCl) — ***J. Phys. Chem. Sol.*** **46 N°10 1185-1193 (1985)**

43 P.V., C.C. — **Evaluation des propriétés thermodynamiques molaires des wüstites solides à partir de leur étude thermogravimétrique à l'équilibre (Evaluation of the molar thermodynamic properties of solid wüstites from their equilibrium thermogravimetric study)**

Première partie : Formulation des grandeurs molaires partielles et intégrales des trois W_i et des trois W'_i (***Part I:*** Formulas for partial and integral molar properties of the three W_i and three W'_i)
ISSN: 0035-1032/86/03 362 16 ; OCLC: 1871287 — ***Rev. Chim. Miné*** **23 n°3 362-377 (1986)**

Deuxième partie : Frontières des sous-domaines de stabilité des W_i et des W'_i. Conditions aux limites. Résultats numériques (***Part II:*** Boundaries of W_i and W'_i stability sub-domains. Limit conditions of the integrations. Numerical assessments)
ISSN: 0035-1032/86/6 709 26 ; OCLC: 1871287 — ***ibidem*** **23 n°6 709-734 (1986)**

Outline: **Wüstite FeO*x*** (Fe*y*O, $y = 1/x$) P_T =1 atm = 0.1013 MPa, Equilibrium oxygen pressure such as $l' = \log_{10} p(O_2)$ known at T(K) in equilibrium gas flow $CO + ½\, O_2 \leftrightarrows CO_2$.
Isothermal lines $l'(x)$ described by means of equation (9) $l' = (a_i x + c_i)T^{-1} + b_i x + d_i$ i = 1,2,3 ⇒ three subphases W_i at T > 1184 K, equation (50) $l' = (a_i x^2 + c_i x + e_i)T^{-1} + b_i x^2 + d_i x + f_i$ i = 1,2,3 ⇒ three subphases W'_i at T < 1184 K (see coefficients a_i to d_i & a_i to f_i in Tables 1 & 2 p.1186 &1187 in paper **n°27**)

The numerical equations allowing to draw the external boundaries $FeOx_0$ /Fe & $FeOx_1/Fe_3O_4$ of diagrams $l'(1/T)$ and $T(x)$ (see paper **n°51**) are adjusted again. They are required to formulate and assess properties $Y°_i$.

- equations $l'_1(T)$: W_i/Fe_3O_4, T>1433 K, eq (76) ; 1433> T>1184 K, eq (77); W'_i/Fe_3O_4, T<1184 K, eq (79)
- equations $l'_0(T)$: W_i/γ-Fe, T>1184 K, eq (75); W'_i/α-Fe, 919<T<1184 K, eq (80); T<919 K, eq (81)
- T_C (Chaudron point) at the intersection (79) X (81): 865 K or 592°C
- equations $T(x_0)$ and $T(x_1)$: they result from the identification of an equation of type (9) or (50) and an equation $l'_0(T)$ or $l'_1(T)$. The composition at T_C = 865 K is x_C = 1.0701 or y_C = 0.9345

Formulation and assessment of the standard molar properties $Y°_i = x/2\ \bar{Y}'_i(O_2) + \bar{Y}_i(Fe)$: $G°_i$, $H°_i$, $S°_i$, $C°_P(i)$
The partial properties $\bar{Y}'_i(O_2)$ are deduced simply from eqs. (9) and (50) of the isotherms [+ the tabulated properties $Y°_T(O_2)$]. The partial properties $\bar{Y}_i(Fe)$ derived from $\bar{Y}'_i(O_2)$ by integration of the Gibbs-Duhem relation [+ the tabulated properties $Y°_T(Fe)$]. It results
- for the **3 W_i**, eqs. (28)-(43),(34)-(45),(38)-(47),(49)
- for the **3 W'_i**, eqs. (58)-(65),(60)-(66),(62)-(67),(68) or (69)

The integration induces functions $y_i(T)$ which depend on A_o and B_o known from the two-terms equations l'_{oi}**(**T) of the W'_i-W_i/α-γIron boundary. They depend on x_o known then by $T(x_o)$

Refinements in the calculations are inserted to initialize accurately $h'_3(T)$ and $s'_3(T)$, i = 3 [p.714 to 716 ⇒ coefficients Ao and Bo in eq.(86) of the boundary W'_3/α-Fe, then x_o]. Functions $y_i(T)$ are linked also by their differences [eqs. (89),(93), (97),(98),(99)] ⇒ shortcuts in numerical assessment

TABLES IV & V p.723 & 724**: $H°_i$ & $S°_i$ for the W_i** & **W'_i** across the whole domain **(**T∈[1644-865K], y∈[0.9569-0.8345] at 1644 K, y_C = 0.9345 (x_C=1.0700) at T_C = 865 K**)**
TABLES VI & VII p.726 & 727**: $C°_P(i)$** above & below 1184 K on external and internal boundaries
TABLES VIII p.728**: $H°_i$, $S°_i$, $C°_P(i)$ for** wüstites **W_1- W'_1** of composition y_C = 0.9345 from 865 to 1644 K

44 J.-R.G., St.J., J. Orewczyk, J.J. — Contribution to the Study of Substituted Wüstites $Fe_{1-z-y}Me_yO$ (Contribution à l'étude des wüstites substituées $Fe_{1-z-y}Me_yO$) — ***Metalurgia I Odlewnictwo*** **<u>13</u> n°1- 2 43-63 (1987)**

45 St.J., J.Orewczyk, J.-R.G. — Influence of Doping with Ca on Change of Stoichiometric Composition of Wustite (Influence du dopage par Ca sur la non-stoechiométrie de la wüstite) — ***Cryst. Latt. Def. and Amorph. Mat.*** **<u>16</u> 49-53 Gordon & Breach Sci. Ed. (1987)**

46 D.W., Renée Veysseyre, C.C. — Sur les symboles du groupe d'espace d'une wüstite de tri-incommensurabilité cubique et sur les groupes de Bravais de sa famille cristalline dans l'espace euclidien à 6 dimensions (About symbols of the space group of a tri-incommensurate cubic wüstite, and Bravais groups of its crystal family in the 6-dimensional euclidean space) — ***C.R.A.S.*** **<u>305</u> Série II 349-352 (1987)**
http://gallica.bnf.fr/ark:/12148/bpt6k5667672t.image.r=roses.f355.langFR.pagination

47 P.V., C.C. — Propriétés thermodynamiques molaires et transformations dans la magnétite non-stœchiométrique en équilibre avec les wüstites (Molar thermodynamic properties and transformations in the nonstoichiometric magnetite in equilibrium with the wüstites) — ***Rev. Chim. miné.*** **<u>24</u> n°6 719-37 (1987)**

48 J.-R.G. — Sur la stabilité des amas de défauts complexes dans la wüstite à haute température (On the Steady State of Clusters in Wüstite at High Temperature) — ***C.R.A.S.*** **<u>306</u> II 957-62 (1988)**
http://gallica.bnf.fr/ark:/12148/bpt6k5664568n/f963.image.pagination.r=comptes%20rendus%20acad%C3%A9mie%20sciences%20paris%201988.langFR

49 J.-R.G., C.C., D.W. — Réexamen de la structure à clusters des wüstites trempées P' et P" (Reexamination of the cluster structure of quenched wüstites P'and P") with **abridged english version.** — ***C.R.A.S.*** **<u>307</u> II 705-710 (1988)**

Outline: Following a speculative description of the defect structure evolution with composition of quenched Fe1-zO (see paper n°29), the cluster [10/4] with its envelope FeO is envisaged as the most convenient one (see papers n^{os} 48, 50, 51, 53) in the points of view of volume, energy of stabilization, stacking with or without faults, adaptation to the variable composition.
This cluster is used to re-interpret HREM (structure) images of a quenched sample P" [see phases *P'* and *P"* in *"Existence d'une surstructure dans le protoxyde de fer"* J. Manenc, J. Phys. Radium 24 (1963) 447-50], synthetized at 1300°C under CO/CO2 gas flow, then moderately fast quenched, final composition z= 0.098: T. Ishiguro & S. Nagakura, Japan. J. Appl. Phys. 24 N°9 (1985) L 723-L726 (réf. [6]).
The geometrical projections along axes [100] (fig. 2(a)) & [101] (fig. 2(b)) below can be exactly superimposed with images in figures 3 & 4 p. L724 (réf. [6]): identical modulus of vector 5X and edge of square in fig.3 and length of rectangle in fig.4; 8 clusters form a cubic supercell $(5X)^3$, X # a_o. The departure from stoichiometry is then z = 0.096, in the assumption that all vacancies being involved in the clusters.

This commensurate stacking is represented with stacking faults in fig. 1(d) p.708. The space group is **P11 a**: see paper n° **53**, G. Nihoul *et al.,* Acta Cryst. for computing simulation of the corresponding HREM images.

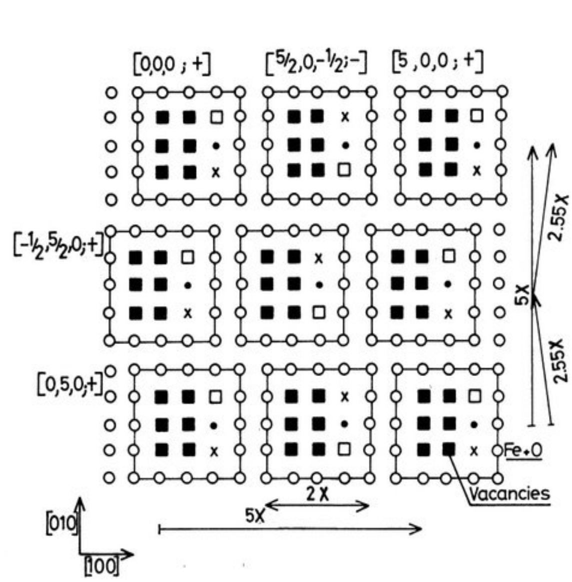


Fig. 2(a)

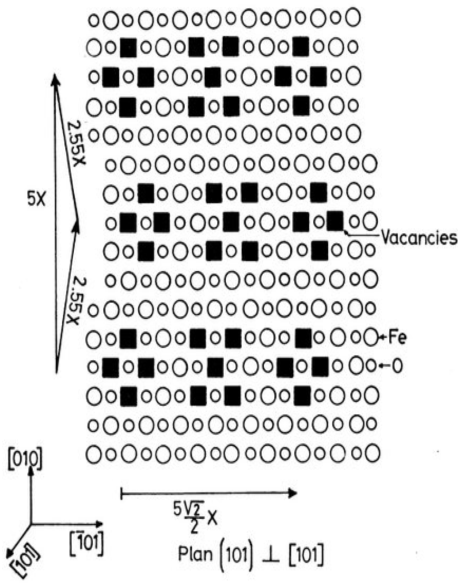


Fig. 2(b)

50 J.-R.G., C.C. — Nucleation and Stability of Defect Clusters: New Energetic Model in the Case of Substituted Wustites (Nucléation et stabilité des amas de défauts : nouveau modèle dans le cas des wüstites substituées) — ***Phase Transitions*** **<u>14</u> 1- 4 103-108 Gordon & Breach Sci. Pub. (1989)**

51 P.V., C.C.

The Fe-O (Iron-Oxygen) Phase Diagram in the Range of the Nonstoichiometric Monoxide (or *wüstite*) **and Magnetite at the Fe-Rich Limit: Reduction Diagrams**
(Diagramme de phases fer-oxygène dans le domaine de composition du monoxyde non-stœchiométrique et de la magnétite en équilibre avec la wüstite : diagrammes de réduction)

Bull. Alloys Phase Diag. **(**=> ***J. of Phase Equilibria)* 10 (3) 209-218 (1989)**

Finalization of phase and subphases (pseudophases) diagram initiated in papers n^{os} 5 and 7 (1963, 1964)
Data to draw the usual *phase diagram T(x)* (from papers n^{os} **27** and **43** Part II). A net of oxygen isobars is drawn. The *reduction diagrams* T(*%H2*) and T(*%CO*) are drawn as charts of metallurgical interest.
An abridged *structural description* of quenched Wi is given following Gavarri *et al.*: *speculative evolution* from Fe to Fe3O4 (defect structure, incommensurability, superstructure: papers n^{os} 29, 46, 49-50-53). A commensurate ordering of cluster [10/4] type blende ZnS with stacking faults is proposed concerning the quenched phase P" (see papers n^{os}29,49-53).

[Missing reference: **69Fen**: B.E.F. Fender and F.D. Riley, "Thermodynamic Properties of Fe1-xO. Transitions in the Single Phase Region", *J. Phys. Chem. Solids, 30* (1969) 793-798]

52 C.C, J.-R.G. — Structural Evolution Study of Substituted Wüstites Fe1-z-y (Ca,Mg)y O (Evolution structurale de wüstites substituées Fe1-z-y (Ca,Mg)y O) — ***J. Phys. Chem. Solids*** **<u>51</u> 9 1131-36 (1990)**

53 Geneviève Nihoul, J.-R.G., C.C. — The Commensurate (10/4) Cluster Model in Quenched Wüstite P". New Simulation of HREM Direct Images — ***Acta Cryst.*** **<u>B47</u> 333-337 (1991)**
DOI:10.1107/S0108768190013568

54 C.C., J.-R.G. — About short and long range ordering in wüstites, $Fe_{1-x}O$. Comment on "Defect distribution and the diffuse **X**-ray diffraction pattern of wüstite, $Fe_{1-x}O$" by T.R. Welberry and A.G. Christy *in* ***Phys. Chem. Minerals*** **(1997) 24:24-38** — ***Phys. Chem. Minerals*** **26: 78-80 (1998)**

55 Abstract, Résumé: $(Fe_{Fe})_{1-3z}\,(Fe^{\cdot}_{Fe})_{2z-t}(Fe_i^{\cdots})_t\,(V''_{Fe})_{z+t}\,O_O$

ABSTRACT - The *nonstoichiometric iron monoxide* or *wüstite* FeO_x ($Fe_{1-z}O$, Fe_yO) is described with a new approach by Pierre Vallet and coworkers, from 1961 (P Raccah's thesis, thermogravimetry under equilibrium) to 1998 (C Carel, JR Gavarri). The stability domain (log p_{O_2},T,x) is separated into 2 subdomains by the isothermal line at 911°C. Each of them contains *three subdomains* which define *varieties* or *subphases Wi and W'i (i = 1,2,3)*. Their molar thermodynamic properties are assessed. An analysis of a reduction kinetics study evidences three separate diffusion processes above 911°C. Following Vallet's approach, the analysis of results of emf measurements leads to a description of the stability domain of *manganese monoxide* or *manganosite* ($Mn_{1-z}O$) with the existence of 5 subphases.

Sets of measurements of the cell parameter after quenching and under equilibrium as a function of x and T show three variations with intersections at thermodynamically forecast values. The *point defect cluster* [10 octahedral vacancies / 4 tetrahedral Fe^{3+}] with blende ZnS structure appears as the most likely in quenched wüstite (JR Gavarri, D Weigel). An *energetic stability model* is proposed taking into account the presence of Ca^{++} or Mg^{++}. *Quenched phase P'* (ex W_1) is described as a modulated cubic tri-incommensurate lattice $(pX)^3$ where 2.5< p <2.7 is irrational. *Quenched phase P"* (ex W_2-W_3) is described as a superstructure with stacking faults (5X, 5X, 2.5X) of cubes formed of clusters [10/4] with their distorted FeO envelope.

The *Cluster Component Method* (A N Men) allows a tensor modeling of the Wi defect ordering by means of elemental components of the most general spinel lattice (more numerous defects near the Fe rich limit).

RÉSUMÉ - Le *monoxyde non-stœchiométrique de fer* ou *wüstite* FeO_x ($Fe_{1-z}O$, Fe_yO) est décrit de façon renouvelée par Pierre Vallet et coll., de 1961 (thèse de P Raccah, thermogravimétrie à l'équilibre) à 1998 (C Carel, JR Gavarri). Le domaine de stabilité (log p_{O_2},T,x) est séparé en 2 sous-domaines par l' isotherme à 911°C. Chacun d'eux l'est en *trois sous-domaines*, définissant des *variétés* ou *sous-phases Wi et W'i (i =1,2,3)*. Leurs grandeurs thermodynamiques molaires sont calculées. Une analyse de résultats de cinétique de réduction montre trois régimes de diffusion distincts au-dessus de 911°C. L'analyse façon Pierre Va llet de résultats de mesures de fem conduit à une description à 5 sous-phases du domaine de stabilité du *monoxyde de manganèse* ou *manganosite* ($Mn_{1-z}O$).

Des ensembles de mesures du paramètre de maille après trempe et à l'équilibre en fonction de x et T indiquent trois variations avec des intersections aux valeurs prévues thermodynamiquement. L'*amas de défauts ponctuels* [10 lacunes octaédriques / 4 Fe^{3+} tétraédriques] de structure blende ZnS apparaît comme le plus probable dans la wüstite trempée (J.-R. Gavarri, D. Weigel). Un *modèle de stabilité énergétique* est proposé prenant en compte la présence de Ca^{++} et Mg^{++}. *La phase trempée P'* (*ex* W_1) est décrite selon un réseau modulé cubique tri-incommensurable $(pX)^3$ où 2,5< p <2,7 est irrationnel. *La phase trempée P"* (*ex* W_2-W_3) est décrite comme une surstructure à défauts d'empilement (5X, 5X, 2,5X) de cubes formés d'amas [10/4] et de leur enveloppe FeO déformée.

La *Méthode de Composition des Amas* (A.N. Men) fournit une modélisation tensorielle de l'ordre des défauts dans les Wi au moyen de motifs élémentaires du réseau spinelle le plus général (défauts plus nombreux près de la frontière W/Fe).
