JOURNAL OF MATERIALS SCIENCE 22 (1987) 4181–4189

Review

Defect structure and transport properties of non-stoichiometric ferrous oxide

S. MROWEC, A. PODGÓRECKA
Institute of Materials Science, Academy of Mining and Metallurgy, Al.Mickiewicza 30, 30-059 Kraków, Poland

The defect and transport properties of ferrous oxide are discussed on the basis of experimental and theoretical work published in the literature. It is shown that extensive defect aggregation in the wustite phase, based on 4:1 clusters, is now a well-established phenomenon. On the other hand, the diffusion mechanism is much more controversial. Some authors assume that diffusional transport of iron ions occurs by means of a non-dissociative mechanism, while others suggest diffusion via free vacancies dissociated from the clusters.

1. Introduction

The physical and chemical properties of ferrous oxide (wustite) have attracted continuous attention for more than sixty years. This unflagging interest results from both practical and cognitive reasons. Wustite constitutes, for instance, the main part of the oxide scale on iron and iron-based alloys, and plays an important role in the reduction processes of iron ores. The extremely large homogeneity range of this oxide, in turn, results in very high, and consequently complicated, electronic and ionic disorder. The defect and transport properties of wustite are, then, the object of extensive experimental studies and theoretical consideration. However, in spite of the enormous number of papers dealing with these problems, there are still many controversial points concerning both the defect structure and the diffusion mechanism in the wustite phase. It seems then of interest to review the literature concerning the defect and transport properties of ferrous oxide in order to outline the actual status of this area of research.

2. Defect structure

Ferrous oxide is a high-temperature phase with the rock-salt structure [1, 2], which disproportionates into magnetite and iron on cooling below 830 K [3] and, rather surprisingly, the stoichiometric composition lies outside the homogeneity range at normal pressures. For instance, a pressure of 36 kbar is needed to obtain the stoichiometric oxide at 1040 K [4]. The phase field of ferrous oxide has been extensively studied by different authors [3, 5–9], with various experimental techniques, and these results are summarized in Fig. 1. It follows clearly from this diagram how large is the homogeneity range of the wustite phase.

The earliest crystallographic studies [1, 2] revealed that the enormous deviations from stoichiometry result from metal deficit and not from oxygen excess, the predominant defects being cation vacancies. This important conclusion has been fully confirmed in studies of the oxidation mechanism of iron. Using, for instance, an inert marker technique [10] it has been demonstrated that the wustite scale on iron grows due to the outward diffusion of metal [11–15], as shown in Fig. 2.

It is interesting to note that the above-mentioned studies initiated already in 1929 by Pfeil [11] constituted the turning point in established views on the mechanism of metal oxidation, and created an experimental basis for the development of Wagner's theory of scale growth.

In spite of the very high concentration of defects in the wustite phase, exceeding 15 at %, it has been assumed in earlier work [16–20] that cation vacancies in ferrous oxide do not interact and are randomly distributed in the crystal lattice, enabling thus the application of point defect thermodynamics. Such an approach led immediately to the conclusion that the non-stoichiometry should be a linear function of the equilibrium oxygen pressure in a double logarithmic plot, with the slope between 1/2 and 1/6 depending on the degree of defect ionization. The first experimental results [3, 21, 22] on the dependence of deviations from stoichiometry on oxygen pressure appeared to support the assumed simple defect structure model. The data presented in Fig. 3 show clearly the linear relationship between log y and log p_{O_2} with a slope of 1/6, suggesting that the predominant defects in the wustite phase are doubly ionized cation vacancies. However, further extensive thermogravimetric [9, 23–28] and e.m.f. [29–34] studies have demonstrated that the dependence of non-stoichiometry in ferrous oxide on equilibrium oxygen pressure is much more complicated and cannot be explained in terms of a point defect model. For illustration, most representative results of this dependence are collected in Fig. 4. It follows from this plot that the discussed relationship cannot be approximated by a straight line, even in the limited part of the phase field of $Fe_{1-y}O$. In addition,

0022–2461/87 $03.00 + .12 © *1987 Chapman and Hall Ltd.*

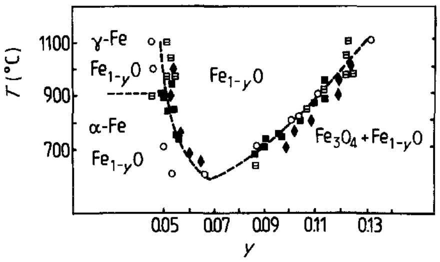

Figure 1 Phase diagram of ferrous oxide. [3, 5–8]. (○) Darken and Gurry [3], (◆) Engell [5], (□) Marion [6], (■) Nowotny and Sikora [8].

from the data presented in Fig. 4 it follows clearly that the non-stoichiometry, and consequently the cation vacancy concentration, decreases with increasing temperature, which is not consistent with a simple defect structure. Rather, strong interactions and clustering of defects could have been expected. This conclusion has been confirmed in subsequent X-ray [35, 36] and neutron diffraction [37–40] studies.

The pioneering work by Roth [37] is of particular importance since it showed for the first time that not only cation vacancies but also interstitial iron ions occur in the cation sublattice of the wustite phase. This was a most surprising discovery, because the coexistence of vacancies and interstitials in non-stoichiometric phases seemed to be extremely unlikely [41]. Using a powder neutron diffraction method on quenched samples Roth [37] has been able to demonstrate that for each cation vacancy which is created as a result of non-stoichiometry, a Frenkel defect pair is simultaneously formed by the transfer of a trivalent octahedral iron ion to a tetrahedral interstitial site. This implies that the real concentration of cation vacancies in ferrous oxide is about twice that resulting from non-stoichiometry, reaching thus the enormous value of about 30 at %. To rationalize these results, Roth [37] proposed that the interstitial cations together with cation vacancies form extended defects, subsequently known as Roth complexes. Such a defect cluster, presented schematically in Fig. 5, consists of two octahedral cation vacancies and one trivalent iron ion in a tetrahedral position, being thus characterized by the vacancy-to-interstitial ratio $R_{VI} = 2$.

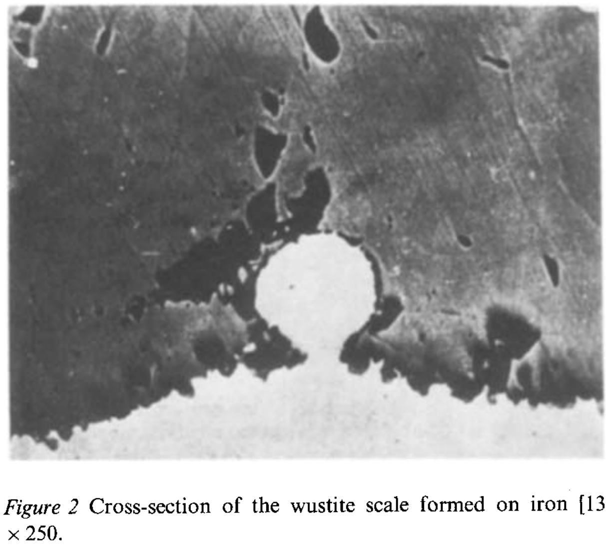

Figure 2 Cross-section of the wustite scale formed on iron [13] × 250.

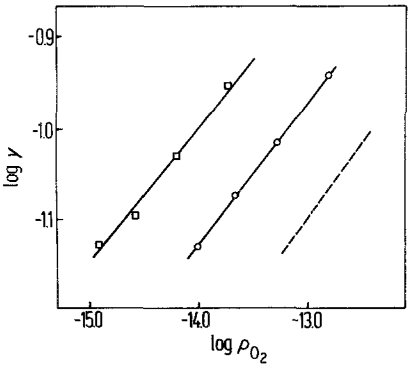

Figure 3 The dependence of nonstoichiometry y in $Fe_{1-y}O$ on equilibrium oxygen pressure [21]. (□) 950° C, (○) 1000° C, (– – –) $y \sim p_{O_2}^{1/6}$.

Kofstad and Hed [42] treated this problem in terms of defect thermodynamics, assuming the formation of neutral and singly ionized Roth complexes. The agreement between the calculated and experimental dependence of non-stoichiometry on oxygen pressure was quite satisfactory, as can be seen in Fig. 6. These results seemed then to support the defect structure model based on Roth complexes. However, at the end of the 1960s much more detailed diffraction studies using single crystals were reported by Koch and Cohen [36]. This work confirmed the qualitative feature of Roth's study concerning the coexistence of vacancies and interstitials; however, the vacancy-to-interstitial ratio R_{VI}, was found to be definitely higher than two (~ 3.2), suggesting that the Roth cluster is an oversimplified model of the defect structure of $Fe_{1-y}O$. These authors derived a large, high-symmetry cluster, called a Koch–Cohen cluster, with $R_{VI} = 3.25$, consisting of thirteen octahedral cation vacancies and four tetrahedral plus three interstitial cations, as shown schematically in Fig. 7. It follows from this diagram that the formation of the Koch–Cohen clusters is associated with a considerable aggregation of cation vacancies. In fact, within the cluster there are no iron ions in octahedral positions, since all 13 cation sites of the wustite lattice in this fragment of the crystal structure are empty.

In the same period of time Vallet and Raccah [9, 43], as well as Kleman [44] and Fender and Riley [33], on the basis of thermogravimetric and e.m.f. studies of non-stoichiometry as a function of equilibrium oxygen pressure and temperature (Fig. 4), suggested that the ferrous oxide phase field is subdivided at least into three regions labelled W_1, W_2 and W_3 which are separated by second- or higher-order phase transitions. These subphase fields are indicated in Fig. 8. Fender and Riley [33] proposed that the transition from one region to another was due to order–disorder transitions, and that subphases W_1, W_2 and W_3 represented increasing order. Further evidence for these subphases appeared to be obtained by Carel and coworkers [46–49] who measured the lattice parameter of the wustite phase as a function of its composition, as well as dilatometric effects. Using these and further experimental results [49] Vallet and Carel [47] proposed a more elaborated phase diagram for the wustite phase as shown in Fig. 9. It follows from this

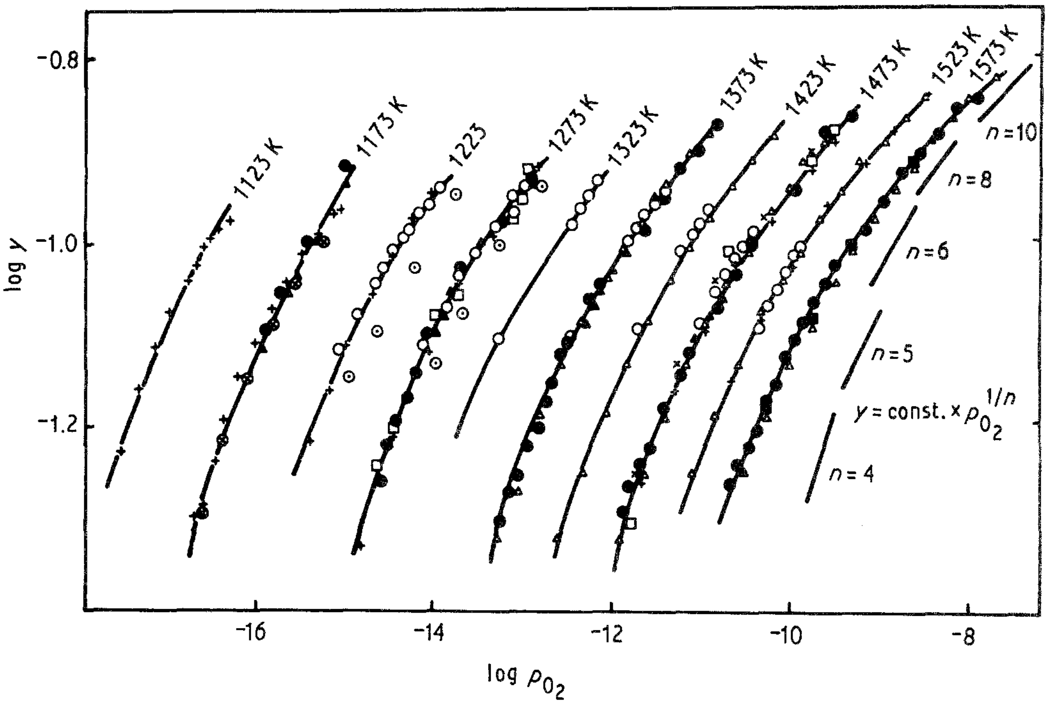

Figure 4 The dependence of non-stoichiometry y in $Fe_{1-y}O$ on equilibrium oxygen pressure for several temperatures: (●) Bransky and Hed [27]; (□) Chen and Peterson [65]; (■) Darken and Gurry [3]; (▲) Fender and Riley [33]; (⊙) Hauffe and Pfeiffer [21]; (⊗) Picard and Dode [70]; (x) Sockel and Schmalzried [30]; (○) Swaroop and Wagner [26]; (△) Takayama and Kimizuka [28]; (+) Vallet and Raccah [43].

plot that the division of the phase field into three regions is slightly different above 910° C than below this temperature. Consequently, six subphases have finally been suggested.

However, this interesting hypothesis has not been accepted in the literature. Lattice parameter measurements and diffraction experiments have produced no supportive evidence. The most precise measurements carried out by Hayakawa *et al.* [50] on single-crystalline material in equilibrium conditions have shown explicitly that the lattice parameter of the wustite phase is a linear function of its composition and decreases continuously with increasing non-stoichiometry (Fig. 10). This parameter changes also continuously with temperature (Fig. 11). If the subphases really exist, the slopes of the plots of the lattice parameters against composition (Fig. 10) or temperature (Fig. 11) would change at the subphase boundaries. No such phenomenon has been observed.

The possible existence of subphases in the wustite phase has also been studied by Nowotny and Sikora [51] using a very sensitive work function technique [52]. These experiments, like those of Hayakawa *et al.* [50] have been carried out at high temperatures in equilibrium conditions, and no effect was observed that could be ascribed to structural regions, domains or subphases as postulated by Vallet and Raccah [43], Klemen [44] and Fender and Riley [33]. In all experiments at different temperatures (675 to 950° C) the work function changed continuously with wustite composition over the whole phase field of this compound. For illustration Fig. 12 shows such a dependence at 950° C.

It should be noted also that the results obtained on quenched wustite scales strongly support the above conclusion. It has been shown, for instance, that the lattice parameter of $Fe_{1-y}O$ scale formed on iron at 880° C decreases smoothly with increasing distance from the metal–scale interface [53], as indicated in Fig. 13. Also, non-stoichiometry of the wustite scale increases continuously with increasing distance from the $Fe{-}Fe_{1-y}O$ phase boundary [54], as can be seen in Fig. 14. Finally, recent detailed thermogravimetric measurements [28] of the wustite composition as a function of equilibrium oxygen pressure and

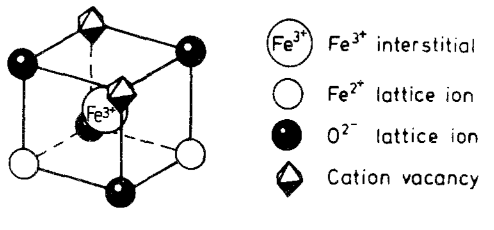

Figure 5 Interstitial-vacancy cluster of 2 : 1 type proposed by Roth [37].

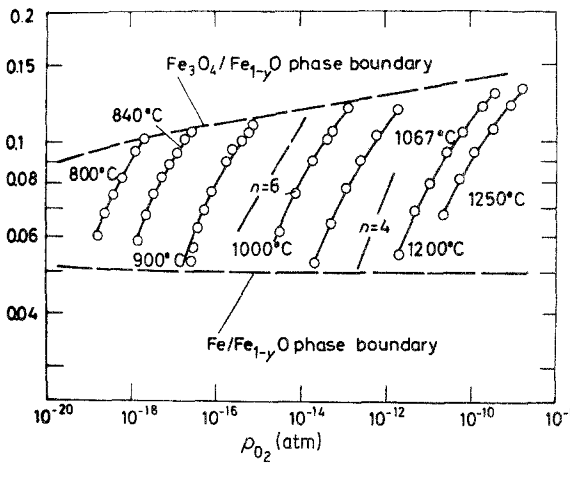

Figure 6 The dependence of non-stoichiometry y in $Fe_{1-y}O$ on equilibrium oxygen pressure for several temperatures [42]. Solid lines show calculated dependence. Experimental points after Vallet and Raccah [9].

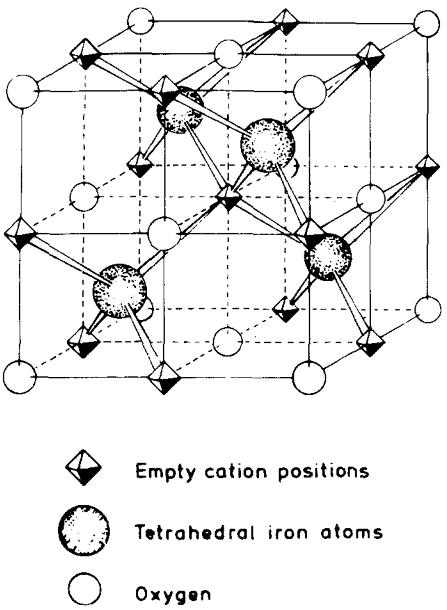

Figure 7 High-symmetry cluster of corner-sharing tetrahedra proposed by Koch and Cohen [36].

temperature, carried out especially in order to verify the division of the wustite phase field into several subphases, gave no clear indication of the existence of any subphase. Fig. 15 shows for illustration the determined dependence of non-stoichiometry of the wustite phase on oxygen pressure for several temperatures in a semi-logarithmic system of coordinates. It follows from this plot that the authors tried to find some discontinuities in this dependence, corresponding to appropriate subphase boundaries. However, these discontinuities are rather artificial and do not exceed the experimental error. In addition, only one – if any – subphase boundary has been found with no relation to those proposed by Vallet and Carel [47] as can be seen in Fig. 16. Thus, the question of the existence of subphases in the wustite phase remains open.

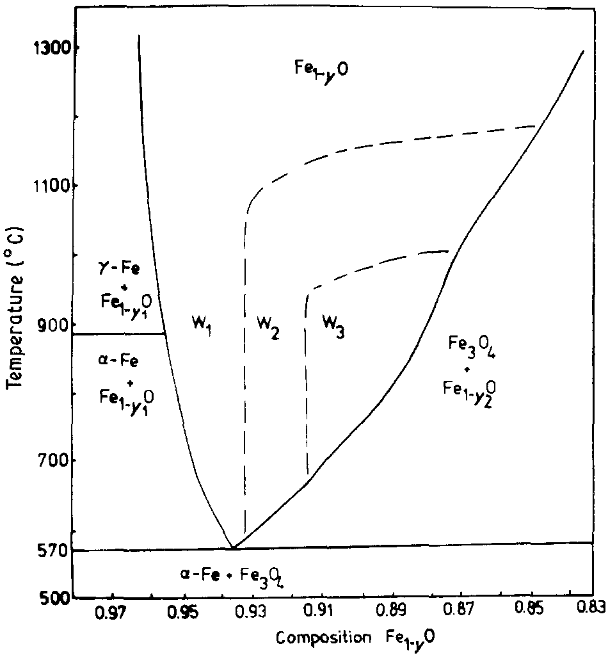

Figure 8 The ferrous oxide phase diagram [45]. Dotted lines indicate subphase boundaries suggested by Vallet and Raccah [9].

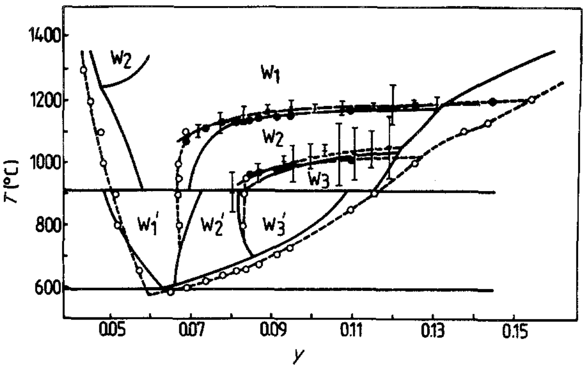

Figure 9 (——) The phase diagram of wustite after Vallet and Carel [47] (lower portion) and Carel and Gavarri [46] (upper portion); (- - -) Fender and Riley [33]; (-–) Carel *et al.* [61].

The next important step forward has been made by Cheetham and co-workers [38, 39] who used an improved neutron diffraction technique in studying the relative populations of vacancy and interstitial sites in the wustite phase. It has been shown that the vacancy-to-interstitial ratio varied with non-stoichiometry between 3 and 4, reaching a maximum value at the Fe–Fe$_{1-y}$O phase boundary, i.e. at the lowest defect concentration. These results strongly suggested the existence of different types of defect cluster as a function of oxide composition and temperature. The question then arose of how defect aggregation stabilizes interstitials, and how does the cluster structure change with non-stoichiometry. The next important question concerned the extent of the deviations from stoichiometry that are necessary for clustering to occur. All these problems were extensively studied by Catlow and co-workers [41, 55–59] by means of a modern computer simulation technique, based on a generalized Mott–Littleton procedure. It was shown that interstitial cations are stabilized essentially by Coulomb interactions with a surrounding vacancy aggregate. Conversely, vacancy aggregation – an unusual process involving the clustering of defects of like charge – is made possible by interstitial formation. Consequently, vacancy aggregation in Fe$_{1-y}$O is an energetically favourable process, provided that interstitials are created within the vacancy aggregate. A 4:1 cluster, consisting of four octahedral cation vacancies surrounding one plus three tetrahedral

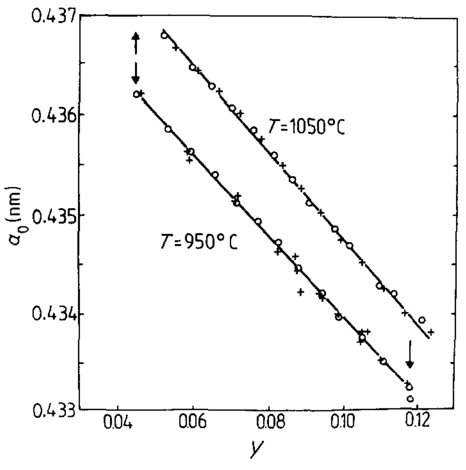

Figure 10 The dependence of the lattice parameter of the wustite phase on its composition at 1050 and 950° C [50].

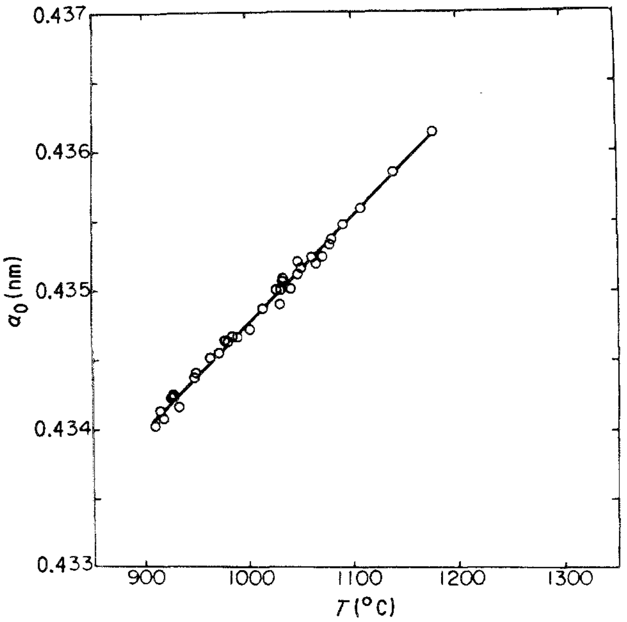

Figure 11 The dependence of the lattice parameter of the wustite phase on temperature [50]. CO = 34%.

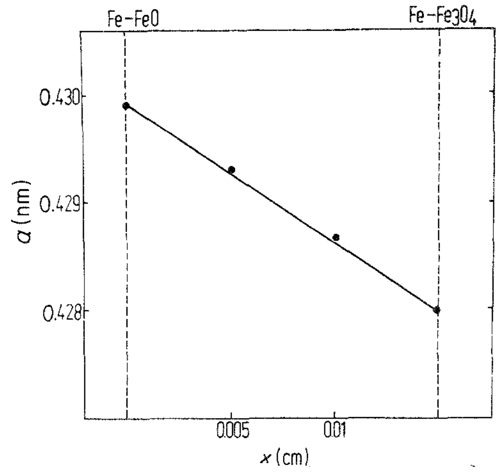

Figure 13 The dependence of the lattice parameter of the wustite scale formed at 880° C on the distance from the Fe–$Fe_{1-y}O$ interface [53].

interstitial cations, was found to be strongly bound with respect to isolated vacancies, and was shown by the calculations to be the basic unit of the defect structure of ferrous oxide. The scheme of this cluster is shown in Fig. 17. It is interesting to note that this cluster is consistent with a much larger 13:4 Koch–Cohen complex (Fig. 7) which can be considered as built from four 4:1 clusters.

Catlow and co-workers [55–60] showed further that the aggregation of 4:1 clusters is an energetically favourable process. It was demonstrated that the initial mode of this process involves the formation of edge-shared aggregates – principally 6:2, 8:3 and 12:4 clusters. Greater defect assemblies form rather by corner-sharing 4:1 clusters (Fig. 18). Initial aggregation by edge sharing is thus replaced by the formation of larger corner-shared clusters with possible spinel nucleation. A 16:5 cluster is, for instance, an element of the inverse spinel structure adopted by Fe_3O_4 and can thus be considered as a nucleus of this ordered structure. It should be stressed that this model of defect aggregation is in full agreement with the experimentally determined dependence of vacancy-to-interstitial ratio on non-stoichiometry. Cheetham *et al.* [38] showed, for instance, that the R_{VI} ratio decreases from 4 to 3 with increasing deviations from stoichiometry, which is equivalent with the formation of 4:1 clusters at low defect concentrations and with further aggregation as the vacancy concentration is raised.

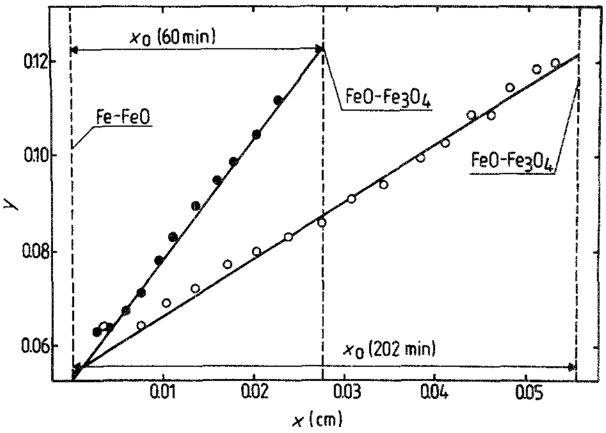

Figure 14 The dependence of non-stoichiometry in the wustite scale formed at 900° C on the distance from the metal–scale interface [54]: (●) oxidation time 60 min, (○) 202 min.

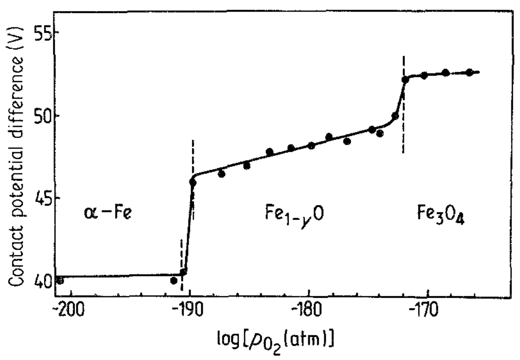

Figure 12 Contact potential difference (directly proportional to the work function of electrons) as a function of equilibrium oxygen pressure for the wustite phase at 800° C [51]. Vertical dotted lines mark Fe–$Fe_{1-y}O$ and $Fe_{1-y}O$–Fe_3O_4 phase boundaries according to Engel [54].

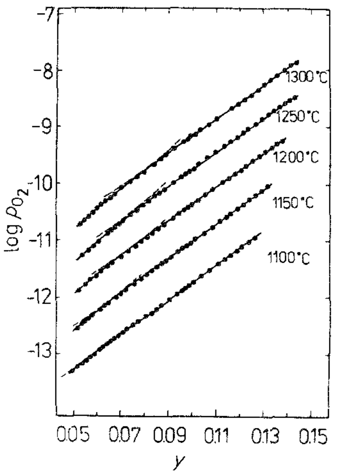

Figure 15 The dependence of non-stoichiometry y in $Fe_{l-y}O$ on equilibrium oxygen pressure for several temperatures [28].

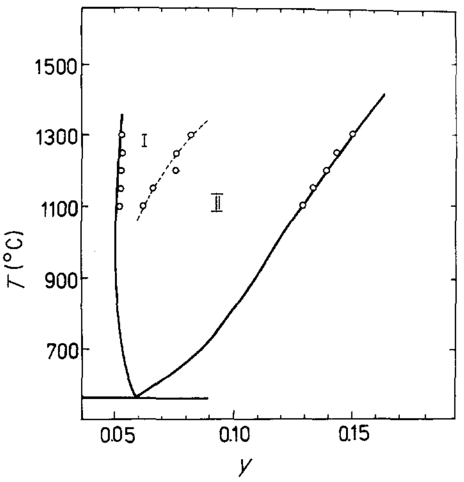

Figure 16 (○) The phase diagram of the wustite phase after Takayama and Kimizuka [28] and (——) Darken and Gurry [3]. The subphase boundary is marked by the dotted line.

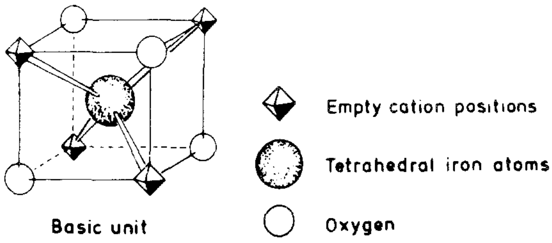

Figure 17 Interstitial-vacancy cluster of 4:1 type proposed by Battle and Cheetham [39] and Catlow *et al.* [59].

A final important problem considered recently by Tomlison *et al.* [59] concerned the critical concentration of cation vacancies in the wustite phase, above which the clustering of defects becomes significant. Appropriate calculations showed clearly that the transition from a defect structure, dominated by isolated vacancies and electron holes, to one in which the 4:1 clusters begin to predominate is strongly temperature-dependent and at 1600 K the clustering of defects is to be expected for the non-stoichiometry $y \geqslant 10^{-2}$. This critical value is lower than the minimum deviation from stoichiometry if $Fe_{1-y}O$ is in equilibrium with iron, being approximately equal to 5×10^{-2} (Fig. 1). It means that over the whole phase field of $Fe_{1-y}O$ the disorder of this oxide is dominated by defect clusters. This important conclusion is directly related to the transport properties of the wustite phase.

3. Transport properties

From the above discussion it follows clearly that the occurrence of extensive defect aggrgation in the wustite phase, based on 4:1 clusters, is now a well-established phenomenon. On the other hand, the diffusion mechanism is much more controversial. Early work [61–63] indicated that the self-diffusion coefficient of iron in $Fe_{1-y}O$ increases with non-stoichiometry as can be seen in Fig. 19. The activation energy of diffusion has also been found to increase with increasing deviations from stoichiometry [64] as shown in Fig. 20. The dependence of this parameter on the non-stoichiometry of the wustite phase is presented in Fig. 21. These observations indicated that the iron ions did not diffuse by a simple vacancy mechanism consisting of successive jumps to neighbouring vacancies, randomly distributed in the crystal lattice. It should be noted that at constant oxygen pressure the diffusion rate of iron in ferrous oxide *decreases* with increasing temperature, as shown in Fig. 22. This *a prior* unexpected behaviour was explained by Kofstad [64] to be due to the fact that the defect concentration decreases with increasing temperature to an even larger extent than the mobility of defect increases.

Self-diffusion of iron in ferrous oxide has been again the subject of extensive studies by Chen and Peterson [65]. The experiments were performed very carefully, using high-purity single crystals, and the penetration profiles were followed by a sectioning method whereas most previous work was done with the less reliable surface decrease technique. Also, the isotopic mass

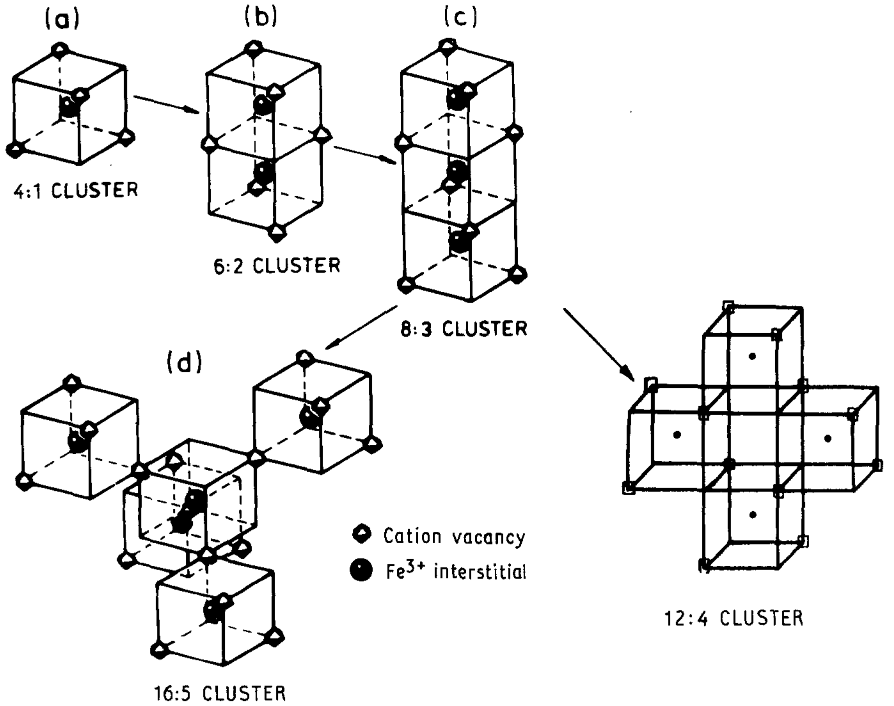

Figure 18 Interstitial-vacancy clusters and clustering scheme in $Fe_{1-y}O$, proposed by Catlow and co-workers [41, 59].

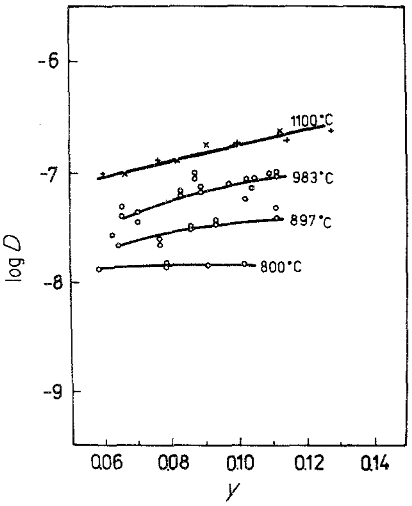

Figure 19 The dependence of the self-diffusion coefficient of iron in ferrous oxide on its composition, for several temperatures: (x) Desmarescaux *et al.* [63]; (+) Hembree and Wagner [62]; (○) ^{55}Fe, Himmel *et al.* [61].

effect was measured by simultaneously applying ^{52}Fe and ^{59}Fe as tracers. The results obtained by Chen and Peterson [65] are at variance to some degree with the data discussed above. The dependence of the self-diffusion coefficient of iron on non-stoichiometry has, for instance, been found to be irregular. As can be seen in Fig. 23 the diffusion rate decreases with increasing non-stoichiometry at lower temperatures (802° C); it is rather insensitive to any change of oxide composition at intermediate temperatures (1003° C) and it increases very slightly with increasing y at higher temperatures (1200° C).

Such a dependence is in contrast to previous results as can be seen in Fig. 24, showing once again the Chen and Peterson data on the background of earlier results obtained by different authors. Fig. 25, in turn, shows the dependence of the isotopic mass effect on oxide composition. As can be seen, $f\Delta K$ decreases with increasing non-stoichiometry, strongly suggesting that the diffusion mechanism is influenced by the clustering of defects.

Chemical diffusion data seem to point out at the same effect. As can be seen in Fig. 26, the chemical diffusion coefficient decreases with increasing deviations from stoichiometry, suggesting that the mobility of defects decreases with an increase in their concentration. In conclusion, Chen and Peterson [65] as well as Matzke [67] assume that iron diffusion in ferrous oxide proceeds most probably via free mobile vacancies coexisting with defect clusters. Thus, only a small fraction of the total vacancies contributes to cation diffusion in $Fe_{1-y}O$. Iron ions diffuse by exchanging sites with free mobile vacancies, and because of the site-blocking effect [68] the mobility of these vacancies decreases with increasing non-stoichiometry.

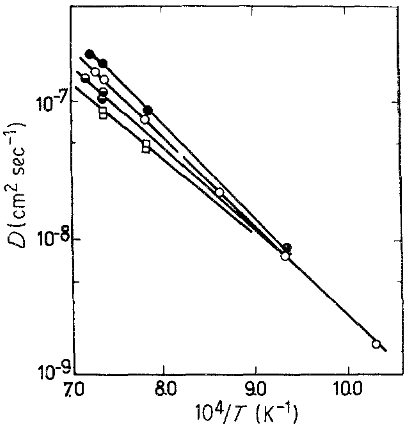

Figure 20 The influence of oxide composition on the temperature dependence of the self-diffusion coefficient of iron in $Fe_{1-y}O$ [63]: y = (●) 0.106, (○) 0.092, (◒) 0.083, (□) 0.067.

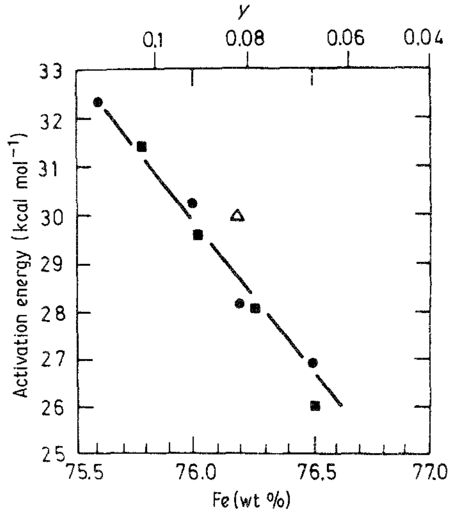

Figure 21 The dependence of the activation energy of self-diffusion of iron in wustite on non-stoichiometry [64]. 1 kcal = 4.1868 kJ.

A different view on the diffusion mechanism of iron in ferrous oxide is represented by Catlow *et al.* [69]. These authors have shown by calculations that the activation energy for jumps of free vacancies in the wustite phase is lower than the cluster binding energy per vacancy. The obvious conclusion was that diffusion cannot occur via free vacancies dissociated from the clusters, but the clusters themselves must move without vacancy dissociation. Considering possible types of such a concerted mechanism of diffusion Catlow *et al.* [69] discussed the migration of 4 : 1

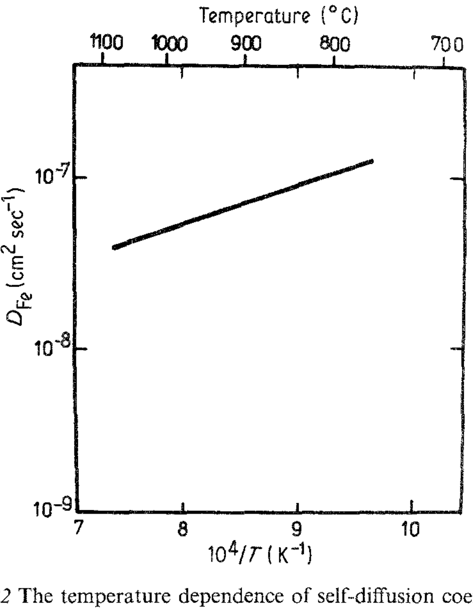

Figure 22 The temperature dependence of self-diffusion coefficient of iron in wustite at constant oxygen pressure [64]; p_{O_2} = 10^{-13} atm.

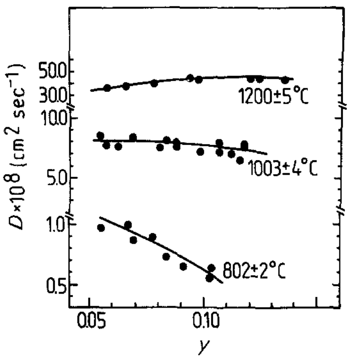

Figure 23 The dependence of self-diffusion coefficient of iron in $Fe_{1-y}O$ on oxide composition for several temperatures [65].

clusters. The model of this mechanism is shown schematically in Fig. 27. The initial step comprises a lattice atom migration towards an interstitial site from one of the nearest-neighbour cation sites surrounding the cluster. The migrating cation then displaces the interstitial cation from the centre of the original 4 : 1 cluster into one of the vacancies present in the cluster. In this step the process passes through the configuration shown schematically in Fig. 27, which is suggested as the saddle point for the whole mechanism of diffusion. The migration process is completed with a second lattice cation moving from a second lattice site and displacing the first migrating cation into another of the vacancies of the original 4 : 1 cluster. Consequently, the 4 : 1 cluster configuration is regenerated, but the extended defect has been displaced by one lattice parameter.

4. Conclusions

From the above discussion it follows clearly that the defect structure and diffusion mechanism in the wustite phase are very complex. In spite of an enormous amount of work many problems remain unsolved. However, extensive X-ray and neutron diffraction studies together with sophisticated theoretical calculations have greatly contributed to a better understanding of the very complicated defect structure of ferrous oxide. Consequently, it is now generally accepted that the defect structure of the wustite is based on aggregates of 4 : 1 clusters. Edge-shared aggregates, 6 : 2, 8 : 3 and 12 : 4 clusters are thought to be most important. The calculations suggest that at high temperatures there is an equilibrium between all types of defect cluster with the nature of the dominant cluster depending on temperature and oxide composition. Indeed, it is distinctly possible that different clusters will dominate in different composition regions, giving rise to the subdivision of the wustite phase which has been the subject of much speculation.

On the other hand, the diffusion mechanism is much more controversial. Catlow and co-workers assume that the diffusional transport of iron ions in the wustite phase occurs by means of a non-dissociative mechanism, i.e. the clusters themselves move without

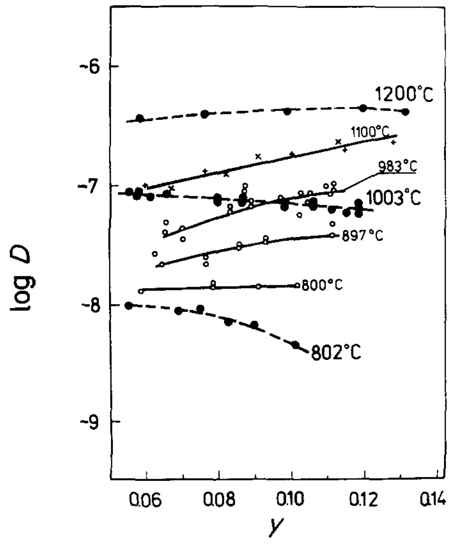

Figure 24 Collective plot of the dependence of self-diffusion coefficient of iron in $Fe_{1-y}O$ on non-stoichiometry for several temperatures. (●) ^{59}Fe, Chen and Peterson [65]; (x) Desmarescaux *et al.* [63]; (+) Hembree and Wagner [62]; (○) ^{55}Fe, Himmel *et al.* [61].

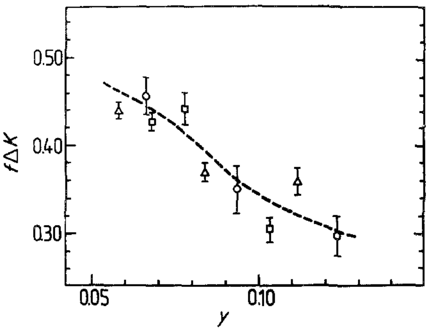

Figure 25 The dependence of the isotopic mass effect, $f\Delta K$, on non-stoichiometry for iron self-diffusion in $Fe_{1-y}O$ [65]: (○) 1203 ± 2°C, (△) 1002 ± 2°C, (□) 807 ± 2°C.

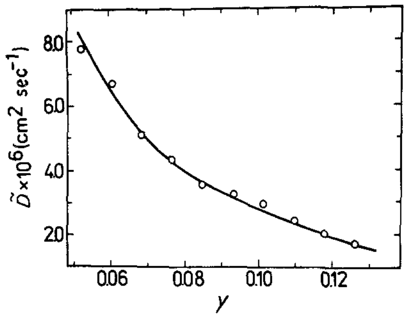

Figure 26 The dependence of chemical diffusion coefficient, $\tilde{D}$, on deviations from stoichiometry, for $Fe_{1-y}O$ at 1100°C [66].

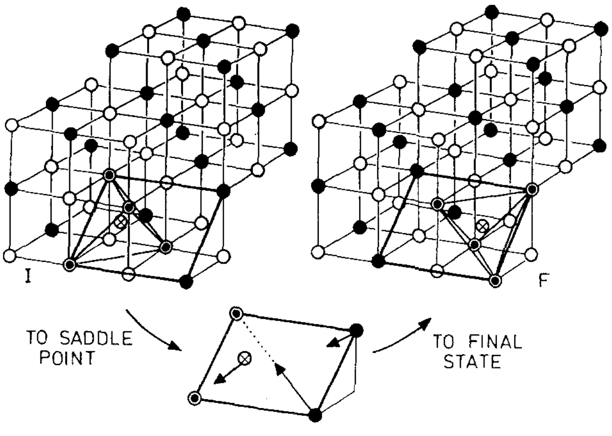

Figure 27 Concerted mechanism for migration of 4 : 1 cluster in ferrous oxide, after Catlow *et al.* [69].

vacancy dissociation. On the other hand, Chen and Peterson as well as Matzke suggest that the self-diffusion of iron in ferrous oxide proceeds via free vacancies dissociated from the clusters. An explanation of all these problems needs much more information, especially on different defect equilibria as a function of temperature and oxide composition.

References

1. R. W. G. WYCOFF and E. D. CRITTENDEN, *J. Amer. Chem. Soc.* **47** (1925) 2876.
2. E. R. JETTE and F. FOOTE, *J. Chem. Phys.* **1** (1933) 29.
3. L. S. DARKEN and R. W. GURRY, *J. Amer. Chem. Soc.* **67** (1945) 1398.
4. T. KATSURA, B. IWASAKI, S. KIMURA and S. AKIMOTO, *J. Chem. Phys.* **47** (1967) 4559.
5. H. J. ENGELL, *Arch. Eisenhüttenwes.* **28** (1955) 109.
6. F. MARION, *Doc. Metall* **24** (1955) 5.
7. G. G. CHARETTE and S. N. FLENGAS, *J. Electrochem. Soc.* **115** (1968) 796.
8. J. NOWOTNY and I. SIKORA, *ibid.* **125** (1978) 781.
9. P. VALLET and P. RACCAH, *Mem. Sci. Rev. Metall.* **62** (1965) 1.
10. S. MROWEC, *Z. phys. Chem. N.F.* **29** (1961) 47.
11. L. PFEIL, *J. Iron Steel Inst.* **119** (1929) 501.
12. *Idem, ibid.* **183** (1931) 237.
13. H. J. ENGELL and F. WEVER, *Acta Metall.* **5** (1957) 695.
14. M. CAGNET and J. MOREAU, *Rev. Métall.* **55** (1958).
15. *Idem, Acta Metall.* **7** (1959) 427.
16. C. WAGNER and E. KOCH, *Z. phys. Chem.* **B32** (1936) 439.
17. L. S. DARKEN and R. W. GURRY, *J. Amer. Chem. Soc.* **68** (1946) 798.
18. D. M. SMYTH, *J. Phys. Chem. Solids* **19** (1961) 167.
19. J. AUBRY and F. MARION, *C. R. Acad. Sci. Paris* **241** (1955) 1778.
20. G. H. GEIGER, R. L. LEVIN and J. B. WAGNER, *J. Phys. Chem. Solids* **27** (1966) 947.
21. K. HAUFFE and H. PFEIFFER, *Z. Metallkde* **44** (1953) 27.
22. J. BRANSKY and D. T. TANNHAUSER, *Trans. AIME* **239** (1967) 75.
23. R. J. ACKERMANN, R. W. SANDFORD, Argonne National Laboratory Report ANL-7250 (1966).
24. R. L. LEVIN and J. B. WAGNER, *Trans. Met. Soc. AIME* **233** (1965) 109.
25. P. F. LANDLER and K. L. KOMAREK, *ibid.* **236** (1966) 138.
26. B. SWAROOP and J. B. WAGNER, *ibid.* **239** (1967) 1215.
27. J. BRANSKY and A. Z. HED, *J. Amer. Ceram. Soc.* **57** (1968) 231.
28. E. TAKAYAMA and N. KIMIZUKA, *J. Electrochem. Soc.* **127** (1980) 970.
29. G. B. BARBI, *J. Phys. Chem.* **68** (1964) 2912.
30. H. G. SOCKEL and H. SCHMALZRIED, *Ber. Bunsenges. phys. Chem.* **72** (1968) 745.
31. H. F. RIZZO and J. V. SMITH, *J. Phys. Chem.* **72** (1968) 485.
32. H. F. RIZZO, R. S. GORDON and J. B. CUTLER, in Proceedings of Symposium on Mass Transport in Oxides, held at Gaithersbury, Maryland, October 1967, edited by J. B. Wachtman and A. D. Franklin, NBS Special Publication No. 296 (National Bureau of Standards, Washington, DC, 1968).
33. B. E. F. FENDER and F. D. RILEY, *J. Phys. Chem. Solids* **30** (1969) 793.
34. R. A. GIDDINGS and R. S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 111.
35. J. SMUTS, *J. Iron Steel Inst.* **204** (1966) 237.
36. F. KOCH and J. B. COHEN, *Acta Crystallogr.* **25** (1969) 275.
37. W. L. ROTH, *ibid.* **13** (1960) 140.
38. A. K. CHEETHAM, B. E. F. FENDER and R. I. TAYLOR, *J. Phys. C* **4** (1971) 2160.
39. P. D. BATTLE and A. K. CHEETHAM, *ibid.* **12** (1979) 337.
40. J. R. GAVARRI, C. CAREL and D. WIEGLER, *J. Solid State Chem.* **29** (1974) 81.
41. C. R. A. CATLOW, in "Nonstoichiometric Oxides", edited by T. Sörensen, (Academic, New York, 1981) p. 61.
42. P. KOFSTAD and A. Z. HED, *J. Electrochem. Soc.* **115** (1968) 102.
43. P. VALLET and P. RACCAH, *C. R. Acad. Sci. Paris* **258** (1964) 3679.
44. M. KLEMAN, *Mem. Sci. Rev. Met.* **62** (1965) 457.
45. A. K. CHEETHAM, in "Nonstoichiometric Oxides", edited by T. Sörensen (Academic, New York, 1981) p. 399.
46. C. CAREL and J. R. GAVARRI, *Mater. Res. Bull.* **11** (1978) 745.
47. P. VALLET and C. CAREL, *ibid.* **14** (1979) 1181.
48. *Idem, Ann. Chim.* **5** (1970) 246.
49. C. CAREL, in Proceedings of Round Table Meeting on Transport and Phase Transformations in Iron and Manganese Oxides, Kraków-Kozubnik, Poland, September 1980 edited by Academy of Mining and Metallurgy, Cracow.
50. M. HAYAKAWA, J. B. COHEN and T. B. REED, *J. Amer. Ceram. Soc.* **55** (1972) 160.
51. J. NOWOTNY and I. SIKORA, *J. Electrochem. Soc.* **125** (1978) 781.
52. *Idem, Bull. Acad. Polon. Sci., Ser. Chim.* **23** (1975) 1045.
53. P. DESMARESCAUX and P. LACOMBE, in Proceedings of 6ème Colloque de Métallurgie, July 1962, edited by C. E. N. Saclay and Presses Univ. de France, Paris (Presses Universitaires de France, Paris, 1962) p. 189.
54. H. J. ENGELL, *Acta Metall.* **6** (1958) 439.
55. C. R. A. CATLOW and B. E. F. FENDER, *J. Phys. C* **8** (1975) 3267.
56. C. R. A. CATLOW, B. E. F. FENDER and D. G. MUXWORTHY, *J. Physique C* **7** (1977) 67.
57. C. R. A. CATLOW and A. M. STONEHAM, *J. Amer. Ceram. Soc.* **64** (1981) 234.
58. C. R. A. CATLOW, R. JAMES, W. C. MACKRODT and R. F. STEWART, *Phys. Rev.* **B25** (1982) 1006.
59. S. M. TOMLISON, C. R. A. CATLOW and J. H. HARDING, in "Transport in Nonstoichiometric Compounds", edited by G. Simkovich and V. S. Stubican (Plenum, New York, 1985) p. 539.
60. C. R. A. CATLOW, in Proceedings of 2nd Round Table Meeting on Physical and Chemical Properties of Wustite and Manganosite, Kraków and Krynica, Poland, September 1983 edited by Academy of Mining and Metallurgy, Cracow, p. 25.
61. L. HIMMEL, R. F. MEHL and C. E. BIRCHENALL, *Trans. AIME* **197** (1953) 827.
62. P. HEMBREE and J. B. WAGNER, *Trans. Metall. Soc. AIME* **245** (1969) 1547.
63. P. DESMARESCAUX, J. P. BOQUET and P. LACOMBE, *Bull. Soc. Chim. Fr.* **15** (1965) 1106.
64. P. KOFSTAD, "Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides" (Wiley–Interscience, New York, 1972) p. 229.
65. W. K. CHEN and N. L. PETERSON, *J. Phys. Chem. Solids* **36** (1975) 1097.
66. J. B. WAGNER, in Proceedings of Symposium on Mass Transport in Oxides", held at Gaithersburg, Maryland, October 1967, edited by J. B. Wachtman and A. D. Franklin, NBS Special Publication No. 296 (National Bureau of Standards, Washington, DC, 1968) p. 65.
67 H. MATZKE, in "Nonstoichiometric Oxides", edited by T. Sörensen (Academic, New York, 1981) p. 211.
68. M. J. DE BRUIN and G. E. MURCH, *Phil. Mag.* **27** (1973) 1475.
69. C. R. A. CATLOW, W. C. MACKRODT, M. J. NORGETT and A. M. STONEHAM, *ibid.* **40** (1979) 161.
70 C. PICARD and M. DODÉ, *Bull. Soc. Chim. Fr.* **7** (1970) 2486.

Received 13 October 1986
and accepted 22 January 1987