# STRUCTURAL EVOLUTION STUDY OF SUBSTITUTED WÜSTITES Fe<sub>1-z-v</sub>(Ca, Mg)<sub>v</sub>O

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(Received 15 February 1990; accepted 20 March 1990)

Abstract—Polycrystalline samples of magnesio- and calciowüstites  $Fe_{(1-z-y)}Me_yO$  with Me = Mg or Ca, were investigated using neutron diffraction experiments. The effective chemical composition was controlled by taking into account Vegard's law for the cell parameters as functions of z and y. The site occupancies were refined: the ratio  $p_{SRO} = (z + t)/t$  was found to increase with increasing Ca substitution while the diffuse scattering of the diffraction patterns decreased. The  $p_{SRO}$  was found to be independent of the level of Mg substitution. The model previously proposed for clustering of defects in pure wüstite is justified: the evolution of the defect structure is interpreted in terms of size effects and surface energy changes of the clusters.

Keywords: Clusters, defect structure, substitution, wüstites, neutron diffraction.

### 1. INTRODUCTION

The non-stoichiometric wüstite  $Fe_{1-2}O$  or:

$$[\mathrm{Fe}_{(1-3z)}^{2+}\mathrm{Fe}_{(2z-i)}^{3+}]^{\mathrm{octa}}[\mathrm{Fe}_{i}^{3+}]^{\mathrm{tetra}}[V_{(z+i)}]^{\mathrm{octa}}\mathrm{O}^{2-}$$

is characterized by a clustering of point defects in a wide range of non-stoichiometry. As previously shown, iron vacancies [V] in the octahedral sites of the face centred lattice are associated with interstitial  $[Fe^{3+}]^{tetra}$  occupying some of the tetrahedral sites. A part of the  $[Fe^{3+}]^{octa}$  in octahedral sites is probably concentrated in the envelope of cubic domains or clusters denoted (m/n) when m vacancies are closely associated with n interstitial cations. Such clusters have been extensively discussed [1-14].

The short range order of point defects can be characterized by the ratio:

$$p_{SRO} = (z+t)/t,$$

where t is the tetrahedral site occupancy and z designates the total iron deficiency.

Taking into account the presence of free vacancies  $(z_{free})$ , this ratio can be related to clusters (m/n):

$$p_{SRO} = m/n + z_{free}/t = 2.4 \pm 0.4$$

for pure wüstite  $Fe_{1-z}O$ .

This last value can be fully explained if one assumes the existence of only one type of cluster denoted (10/4), previously proposed by Anderson *et al.* [11] and recently justified by us [12] and if the concentration  $z_{\text{tree}}$  of free vacancies is low enough.

The new model [12] we proposed for interpreting the existence of cubic clusters such as the (10/4) one of the authors in [11], at high temperature and in a wide range of non-stoichometry, permitted us to predict drastic variations in defect structure upon substitution by cations of large size, such as  $Ca^{2+}$ . A small change in cluster size in the opposite case can also be foreseen upon substitution by  $Mg^{2+}$ .

In the present study, we rely on the structural evolution of such cubic clusters, using neutron diffraction experiments on polycrystalline samples of substituted wüstites denoted  $Fe_{1-2-y}Me_yO$  with Me = Mg or Ca.

#### 2. EXPERIMENTAL

### 2.1. Samples

Polycrystalline samples of magnesiowüstite WMg were prepared in the classic way by heating mixtures of powdered iron, hematite and magnesia for 48 h at 1175°C in sealed evacuated quartz ampoules. After quenching in water, all the samples were characterized by X-ray diffraction to control the final composition and crystallinity. The effects of grinding processes on the diffraction profiles have been systematically studied and published previously [15]. Under certain circumstances, it was shown that a symmetry change may occur after strong grinding of the samples of magnesiowüstites with y < 10% [15].

The polycrystalline calciowüstites WCa were prepared at  $1175^{\circ}$ C using a CO/CO<sub>2</sub> equilibrium atmosphere. The compositions were obtained by extrapolations to  $1175^{\circ}$ C of the stability domain of



Fig. 1. Isothermal section at 1175°C of the stability field of calciowüstite, obtained by extrapolation of Likasov and Kuznetsov's results [16] at 900°C and 1000°C. On the dashed curves the power of 10 of the oxygen pressure (atm) is indicated. Symbols  $(\bullet)$  N designate the sample locations in Table 2. Following Likasov's notation  $(Fe_{1-y}, Ca_y, O_x): x$ = 1/(1-z), y' = y/(1-z).

WCa as determined by Likasov and Kuznetsov [16] (see Fig. 1). Each ceramic sample was coarsely ground. The initial composition z was first calculated from Likasov's data and then refined from diffraction experiments. To do this it was necessary to assume that the Ca/Fe ratio  $\left[ \frac{y}{(1-z-y)} \right]$  was known exactly. Finally, the precise y value had to be confirmed by comparing the observed and modelled cell parameters as discussed below.

## 2.2. Neutron diffraction experiments

The neutron diffraction experiments were carried out at I.L.L. using the diffractometers D1A and D2B. The various diffraction profiles were analysed using the classical Rietveld method [17]. The diffraction patterns were recorded at 300 and 5K over the full angular range  $0-160^{\circ}$  2 $\Theta$ . Only the room temperature measurements are discussed below. The low temperature results were only considered as controlling the thermal evolution of the diffuse scattering clearly observable on the diffraction patterns. The background was removed from the initial diffraction pattern using a classical extrapolation of the undulations due to the defect structure (see Refs 5 and 10). The influence of thermal diffuse scattering was shown not to play a prominent role in such undulations: at low temperature the change in profile can be ascribed to the attenuation factor B alone. This has already been discussed by us [10, 18, 19].

Tables 1 and 2 gather all the structural parameters determined for the WMg and WCa samples, respectively. To interpret the diffraction data, it was necessary to independently determine the concentration z(vacancies), of the effective site occupancies and the effective final y values (Ca or Mg). This was possible by assuming that the cell parameter is a linear function of z and y [19]:

$$a(WMe) = a_0 \cdot [1 - \beta \cdot z] + [a_{MeO} - a_0] \cdot y, \quad (1)$$

where  $a_0 = 4.330$  Å is the cell parameter of stoichiometric wüstite FeO,  $\beta = 0.095$  is obtained from the literature data [19], and  $a_{MgO} = 4.210$  Å and

Table 1. Chemical and structural parameters at 300 K for quenched magnesiowüstites prepared in evacuated sealed tubes at 1 175°C

No. of samples:	1	2(G · S)*	3	4(G · S)*			
Chemical composition $z \times 10^2$ $y_{Mg} \times 10^2$	6.5 7.5	6.5 7.5	8.5 3.0	8.5 3.0			
Number of ( <i>hkl</i> ) $\lambda$ (Å)	7 1.9091†	7 1.9091	7 1.9091	6 1.9091			
Refined $z \times 10^2$ Refined $t \times 10^2$ $p_{SRO} = (z + t)/t$	5.79 (0.5) 3.8 (0.5) 2.53 (0.5)	6.20 (0.5) 3.9 (0.5) 2.54 (0.5)	9.46 (0.6) 5.04 (0.6) 2.88 (0.6)	8.90 (0.6) 6.70 (0.6) 2.33 (0.6)			
Cell parameter (Å) Refined $a_{obs.}$ Ideal $a_{calc}$ ‡ (T = 300 K)	4.2881 (2) 4.297	4.2902 (3)	4.2845 (2) 4.288	4.2853 (3)			
D.W. factors (Å) <sup>2</sup> § B <sub>Fe</sub> B <sub>O</sub> B	0.42 (0.05) 0.69 (0.06) 0.56 (0.06)	0.90 (0.06) 1.10 (0.06) 1.0 (0.06)	0.59 (0.05) 0.77 (0.06) 0.68 (0.06)	0.87 (0.06) 1.20 (0.07) 1.04 (0.07)			
Reliability factor R <sub>N</sub> (%)	2.2	4.5	2.6	2.4			

(G.S)\* = sample studied after standardized grinding (see Ref. 15).

†Experiments on diffractometer DIA in I.L.L. (Grenoble).

 $a_{calc.} = a_W + y_{Mg}[a_{MfO} - a_{FeO}]$  is obtained from relation (1).  $B = (8\pi^2/3) \langle \Delta R^2 \rangle = B_{th}(\Theta) + B_{st}(z)$ , relation (2);  $B_{st}(z) = p \cdot z$  with  $p \sim 4 \text{ Å}^2$  (see Refs 5, 18).

No. of samples:	1	2	3	4	5	6
CO <sub>2</sub> /CO	38.8/61.2	34/66	26.7/73.3	58/42	57/43	58/42
Chemical composition $z \times 10^2$ $y_{Ca} \times 10^2$	6.72 1.0	6.75 3.0	6.48 5.0	8.78 1.0	8.87 3.0	10.1 2.0 <b>‡</b>
Number of $(hkl)$ $\lambda$ (Å)	10 1. <b>5904</b> †	6 1.9091	6 1.9091	6 1.9091	6 1.9091	10 1.5904
Refined $z \times 10^2$ Refined $t \times 10^2$ $p_{SRO}(z + t)/t$	6.88 (0.5) 5.71 (0.5) 2.20 (0.5)	6.49 (0.5) 2.80 (0.5) 3.31 (0.5)	5.34 (0.6) 0.74 (0.5) 8.22 (4.0)	8.50 (0.6) 6.19 (0.5) 2.37 (0.5)	8.99 (0.6) 3.75 (0.5) 3.39 (0.5)	7.10‡ 3.00‡ 3.45 (0.6)
Cell parameter (Å) Refined $a_{obs.}$ Ideal $a_{cak.}$ § ( $T = 300$ K)	4.2979 (2) 4.307	4.3164 (2) 4.318	4.3327 (2) 4.332	4.2950 (2) 4.300	4.3059 (2) 4.307	4.3116 (2) 4.310
D.W. factors (Å <sup>2</sup> ) B <sub>Fe</sub> B <sub>0</sub> B	0.95 (0.05) 1.31 — 1.13 —	0.76 (0.05) 1.33 — 1.05 —	0.73 (0.05) 1.24 — 0.99 —	0.96 (0.05) 1.28 1.12	1.05 (0.05) 1.37 — 1.21 —	1.15 (0.05) 1.40 — 1.28 —
Reliability factor $R_N(\%)$	4.5	3.5	3.5	2.2	3.3	5.1

Table 2. Chemical and structural parameters at 300 K for quenched calciowüstites prepared in CO<sub>2</sub>/CO flows at 1 175°C

†Experiments on diffractometer D2B in I.L.L. (Grenoble).

The global chemical composition was  $y_{Ca} = 0.050$ ; the value  $y_{Ca} = 0.02$  is obtained after adjustment of the calculated value  $a_{cak}$ . to the experimental value  $a_{obs}$ . Values of z and t are refined with fixed values of  $y_{Ca}$ .

 $\$a_{cak} = a_W + y_{Ca}[a_{CaO} - a_{FeO}]$  is obtained from relation (1). Note: for sample No. 3, the value  $p_{SRO} = 8.2 (\pm 4.0)$  is only due to the weak t value: clusters can be assumed to be very dilute or built without occupied tetrahedral sites.

 $a_{CaO} = 4.810$  Å are the cell parameters of MgO and CaO, respectively.

Under these circumstances, the y value is considered as correct when the experimental and modelled cell parameter values are identical. By fixing the y value it was possible to refine the composition value z after substitution. Generally the refined value is found to be close to the expected one, except when small amounts of additional phases (ferrites) are present. The simulated values of the cell parameters are reported in Tables 1 and 2.

The refinement of the Debye-Waller factors confirms all the previous results. The increase of the mean B value as z increases is associated with an increasing quantity of clusters, i.e. with increasing distortions of the mean lattice. Formerly [5, 18], the static component of the B factor was shown to vary as follows:

$$B = B_{\rm th}(T) + B_{\rm st}(z) \tag{2}$$

with  $B_{\rm st}(z) = 4 \cdot z$ .

Thus, for a variation  $z_1 - z_2 = 0.02$  one can expect a variation of 0.08 Å<sup>2</sup> for the static component  $B_{st}$ which is roughly observed from the global *B* values in Tables 1 and 2.

The site occupancy parameters z and t were refined by taking into account the *experimental* values of the cell parameters which allowed us to control the effective compositions y of the samples.

As shown in Table 1, the  $Mg^{2+}$  substituting cations do not affect the ratio (z + t)/t characteristic of the nature of clusters in a significant way. On the contrary, a significant evolution of this ratio is observed in the case of WCa samples: when the Ca concentration  $(y_{Ca})$  increases, the tetrahedral site occupancy (t) decreases thus involving an increase in (z + t)/t. As a consequence, one can conclude that the mean cluster size probably decreases: this evolution is probably accompanied by an increasing concentration of free vacancies distributed in the lattice. For a  $y_{Ca}$  value of 0.05 a very small quantity of interstitial Fe<sup>3+</sup> in tetrahedral sites is observed in Table 2.

Additional information on the short range ordering of point defects was obtained from the undulations clearly present in the diffraction patterns. The integrated intensity of the first diffuse scattering close to the (111) and (200) Bragg peaks, noted as  $I_A$  in Fig. 2, depends on the compositions z and y. The temperature dependence in the 5-300 K range is directly connected with simple thermal attenuation factors which was not the case for the high temperature studies [5] where an evolution of disorder was observed [10]. Using the (111) Bragg peak intensity as the normalizing factor, the intensity of the diffuse scattering  $I_A(z, y)$  was shown to decrease when y increases, while it increases with z, as expected.

The results are reported in Table 3. Figure 3 shows the related evolutions of the short range order parameter (a) and of the modulated structure intensity  $I_A$  (b).

This argues in favour of a dilution of clusters in the lattice in the case of Ca substitution while these clusters might be partly stabilized in the case of Mg substitution. In other words, the modulated



2 theta in degrees

Fig. 2. Neutron diffraction pattern of a polycrystalline WCa (z = 0.065; y = 0.03). The undulation  $I_A$  is indicated. It decreases when the Ca ratio increases.

structure being due to the imperfect arrangement of clusters, the large-sized cation Ca<sup>2+</sup> can modify the next-neighbouring clusters that are locally changed into smaller clusters [e.g. the (4/1) cluster] and free vacancies, thus attenuating the modulated superstructure peaks [21].

### 3. DISCUSSION

Figure 4 gives a simplified representation of (10/4)clusters distributed in the mean cubic lattice with their distorted envelopes in which all the surface energy is assumed to be due only to the elastic distortions of the O-Fe-O bond angles.

In the new model we previously proposed for interpreting the stability of the (10/4) cubic clusters [11, 12], a general expression was found for describing the Gibbs free energy  $G_T$  in the case of mean cubic clusters with their distorted envelopes, considered as nuclei (see Appendix):

$$G_T(N) = -G_V \cdot N^3 + E_S \cdot [0.5N^4 + 1.5N^3 + N^2], \quad (3)$$

where N is an equilibrium size parameter related to the external size of the cubic cluster, including its envelope [12]. By minimizing the free energy  $G_T(N)$ , one obtained a relation giving N as a function of  $G_V$  and  $E_s$ . The terms  $G_V$  and  $E_s$  are the so-called volume and surface energies, respectively. The surface energy is expressed as follows:

$$E_{S} = \langle C_{44} \rangle \cdot v \cdot \langle \delta \alpha_{T} \rangle^{2}$$

where  $C_{44}$  is the elastic shearing constant of the mean cubic structure, and  $\langle \delta \alpha_T \rangle$  is the bound angle distortion associated with lattice accommodations between the cluster domain and the external perfect lattice "FeO". Both quantities depend on the chemical composition  $y_{Me}$  in the case of solid solutions (FeO-CaO, FeO-MgO).

For elastic constants:

$$C^{-1} = (V^{1}/V) \cdot C_{1}^{-1} + (V^{2}/V) \cdot C_{2}^{-1},$$

where the V terms designate the specific volumes of elemental and composite phases. The elastic constants are as follows:  $C_{44}$  (MgO) =  $1.5 \times 10^{11}$  Pa;  $C_{44}$  $(CaO) = 0.8 \times 10^{11} Pa; C_{44}(Fe_{1-z}O) = 0.45 \times 10^{11} Pa.$ For distortions:

$$\begin{aligned} \langle \delta \alpha_T \rangle &= \delta \alpha_0 + \langle \delta \alpha \rangle \\ \langle \delta \alpha \rangle &= y \cdot [a_{\text{MeO}} - a_{\text{FeO}}] / ([a_{\text{FeO}} + a_{\text{MeO}}]/2) \end{aligned}$$

 $\langle \delta \alpha_0 \rangle$  is the angle distortion in pure wüstite Fe<sub>1-2</sub>O.

Table 3.								
No.	Z	Уса	ť	$ F(111) ^2$	$h_{(undul)}/h_{(111)}$	$h_{(undul)}^{\dagger}$		
1	0.069	0.01	0.057	1.0181	0.160	163		
2	0.065	0.03	0.028	1.1616	0.141	164		
3	0.053	0.05	0.007	1.3453	0.100	135		
4	0.085	0.01	0.062	0.8757	0.325	285		
5	0.090	0.03	0.038	0.9033	0.264	238		
6	(0.071)	(0.02)	0.030	1.1394	0.200	228		

 $h_{111} \propto |F_{111}|^2$ .



Fig. 3. (a) Variation of the short range order parameter (z+t)/t with  $y_{Ca}$  in WCa compounds. (b) Variation of the diffuse scattering with  $y_{Ca}$  in WCa compounds (undulation  $I_A$  in arbitrary units).

In the case of WCa compounds the mean elastic constant of the solid solution is expected to vary slowly with composition y; however, the distortion  $\langle \delta \alpha_T \rangle$  can be strongly altered when the Ca content rises to 5%. This is not the case for WMg compounds because the size effect is weaker.

Using elastic data, cell parameters from the literature and direct images of clusters from electron microscopy [20], one can make previsional calculations of the  $E_s$  term. From the direct images [20], one can then introduce the mean equilibrium size value  $(N_m = 5)$  as data permitting the determination of the volume constant  $G_V$ . Finally it is possible to evaluate the optimum size  $N_m$  in the case of substituted wüstites:

$$N_m = [u + (u^2 - 16)^{1/2}]/4,$$

where  $u = 3[G_v/E_s - 3/2]$ .

To determine the  $N_m$  values for compounds WMg and WCa, the sole variable parameter is  $E_s$ , a function of y, the  $G_v$  term being unchanged as a first approximation.



Fig. 4. Representation of clusters (10/4) with their distorted envelopes  $(\langle 100 \rangle$  projection).



Fig. 5. Surface energy term  $E_s$  as a function of the y substitution in the WMg and WCa compounds: for WCa the variation is stronger.

In Fig. 5 the theoretical variations of the surface energy are presented for WCa and WMg compounds. In Fig. 6 the expected variations of  $N_m$  are reported. One observes a drastic variation in the mean cluster size for the WCa compounds with the clusters vanishing at approx.  $y_{Ca} = 0.13$ .

For pure wüstite  $Fe_{0.93}O$  the present model was calibrated using the probable value  $N_m = 5$ which corresponds to a cubic cluster (10/4). One can thus calculate a free energy per vacancy of -0.80 eV in assuming that the cluster is of the (10/4) type as proposed by [11]. For a composition  $y_{Ca} = 0.05$  the equilibrium size  $N_m$  is expected to decrease down to 3.3. In this case the free energy per vacancy can be evaluated to -0.5 eV when the clusters are assumed to be of the (4/1) type.



Fig. 6. Equilibrium size  $N_m$  as a function of y in the WMg and WCa compounds; for WCa the decrease in size is stronger. A critical value ( $y_{Ca} = 0.13$ ) can be evaluated.

A similar energy value was obtained by [11] for the same cluster types.

In the case of WMg compounds, for a composition  $y_{Mg} = 0.05$ , the changes in  $N_m$  and the free energy are rather small, in good agreement with the experimental features found in the literature and here confirmed.

### 4. CONCLUSION

The present neutron diffraction study has shown that the defect structure in substituted wüstites can be strongly modified when the size effect of substituting cations is sufficiently important.

In the case of Ca substituting cations, the nature of the clusters is clearly modified. As long as the defect structure in pure wüstites  $Fe_{1-2}O$  can be described by more or less disordered clusters (10/4) with a modulated structure varying with the composition z, substitution by  $Ca^{2+}$  involves a dilution of such large clusters and an increase of the free vacancy ratio. As a consequence, drastic changes in diffusional properties are expected to be observed. This could explain the diametrically opposite influences of Mg and Ca in iron metallurgy processes, especially in black furnace technology.

Acknowledgements—We gratefully acknowledge Dr A. W. Hewat of the Laue Langevin Institute (Grenoble) for local assistance during experiments.

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### APPENDIX: THE CLUSTER ENERGY MODELLING

The total Gibbs free energy  $G_T(N)$  of a complex cluster including its envelope is a function of the mean number of Fe-O bonds N:  $G_T(N) = -G_V \cdot N^3 + G_S(N)$  where  $G_S(N)$  is the surface free energy. This energy can be calculated for an ideal cubic envelope of a cubic cluster as follows:

$$G_{S} = \sum_{ij} 1/2 \cdot C_{44} \cdot (\delta \alpha)^{2}_{ij} \cdot \nu_{0}$$
$$= \sum 1/2 \cdot C_{44} \cdot [i^{2} + j^{2}] (\delta \alpha_{0})^{2} \cdot \nu_{0}.$$

The summation over the six faces of the cube is obtained between the hypothetical boundary values -N/2, +N/2where N designates the external dimension of the cube expressed in chemical bonds. One uses the relation:

$$\Sigma i^2 = 1 + 2^2 + 3^2 + \dots + (N/2)^2$$
  
= 1/6[(2 \cdot N/2 + 1)(N/2 + 1) \cdot (N/2)].

One obtains for  $G_s$ :

$$G_{S}(N) = \sum_{i} \frac{1}{2} \cdot C_{44} \cdot v_0 \times 2 \times 6 \times N \times 2 \times (\delta \alpha_0)^2 \cdot i^2$$
$$= [v_0 \cdot C_{44} \cdot (\delta \alpha_0)^2] \cdot [1/2N^4 + 3/2N^3 + N^2].$$

The surface term:  $E_s = \langle C_{44} \rangle \cdot v_0 \cdot (\delta \alpha_0)^2$  is generated by the elastic distortions in the cubic envelope of the cluster due to the accommodations between the ionic sizes in the cluster core (vacancies and Fe<sup>3+</sup>) and those of the external pure lattice (only Fe<sup>2+</sup>). After optimization of the free energy one obtains the minimum value as a function of the mean size of the clusters  $N_{m}$ :

$$G_T(N_m) = E_S \cdot (-1/6 \cdot N_m^4 + 1/3 \cdot N_m^2).$$

The distortions can be evaluated from the cell parameters of the associated oxides FeO,  $Fe_2O_3$  for the pure wüstites; the change in distortion by the substitution is governed by the change in ionic sizes. For substituted wüstites:

$$(\delta \alpha_T) = (\delta \alpha)_0 + y \cdot [a_{\text{MeO}} - a_{\text{FeO}}]/\langle a \rangle.$$