substance: FeO ($Fe_{1-x}O$)
property: defects

Review: [80B]. It is established that the predominant type of defect arises from the migration of iron as Fe^{3+} to an interstitial tetrahedral site. To minimize cation repulsion, Fe^{2+} vacancies then cluster in a tetrahedral arrangement around Fe_i^{3+}. The elementary defect is thus Fe_i^{3+} $(V_{Fe}'')_4$. Such a defect is strongly negatively charged and will attract octahedral site Fe^{3+} ions [75C, 77C]. Some suggested defect morphologies are shown in Fig. 1. Calculations favour the 6:2 and 8:3 clusters and neutron diffraction data [71C, 79B, 79G] suggest that the ratio $[V_{Fe}'']/[Fe_i^{3+}]$ does fall from 4 towards 3 with increasing x. X-ray diffraction [69K, 73H] and electron diffraction [74I, 77A] on annealed samples show ordered arrangements of 13:4, 10:3 or 16:6 clusters in a low symmetry structure. The present interpretation of the available experimental evidence is against the formation of corner-shared spinel-like aggregates (Fig. 2) [79G, 77C].

Deviation from stoichiometry vs. oxygen partial pressure: Fig. 3. No simple defect model can fit the data. [68K] suggests the complex defect $Fe_c = Fe_i^{3+}$ (V_{Fe}'') (V_{Fe}') with the following equilibrium reactions:

$Fe_{Fe} + V_i + 1/2\ O_2 \leftrightarrow Fe_c + O_O$, $\quad K_1 = 1.75\cdot10^{-9}\ \exp(79400[\text{cal mol}^{-1}]/RT)$

$Fe_c + Fe_{Fe} \leftrightarrow Fe_c' + Fe_{Fe}\cdot e^+$, $\quad K_i = 0.13\cdot10^{2}\ \exp(-17900[\text{cal mol}^{-1}]/RT)$

Fe_c and Fe_c' are neutral and singly ionized complex defects, respectively. V_i represents an interstitial site available for occupancy by the complex defect, Fe_{Fe} is a divalent Fe atom on a normal site, $Fe_{Fe}\cdot e^+$ atom is a Fe atom on an octahedral site with one trapped hole (a trivalent Fe ion) and O_O is an oxygen atom on an oxygen lattice site. K_1: equilibrium constant for the formation of neutral complex species, K_i: equilibrium constant for the first ionization.

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Fig. 1.

$Fe_{1-x}O$. Different defect clusters proposed [80B].

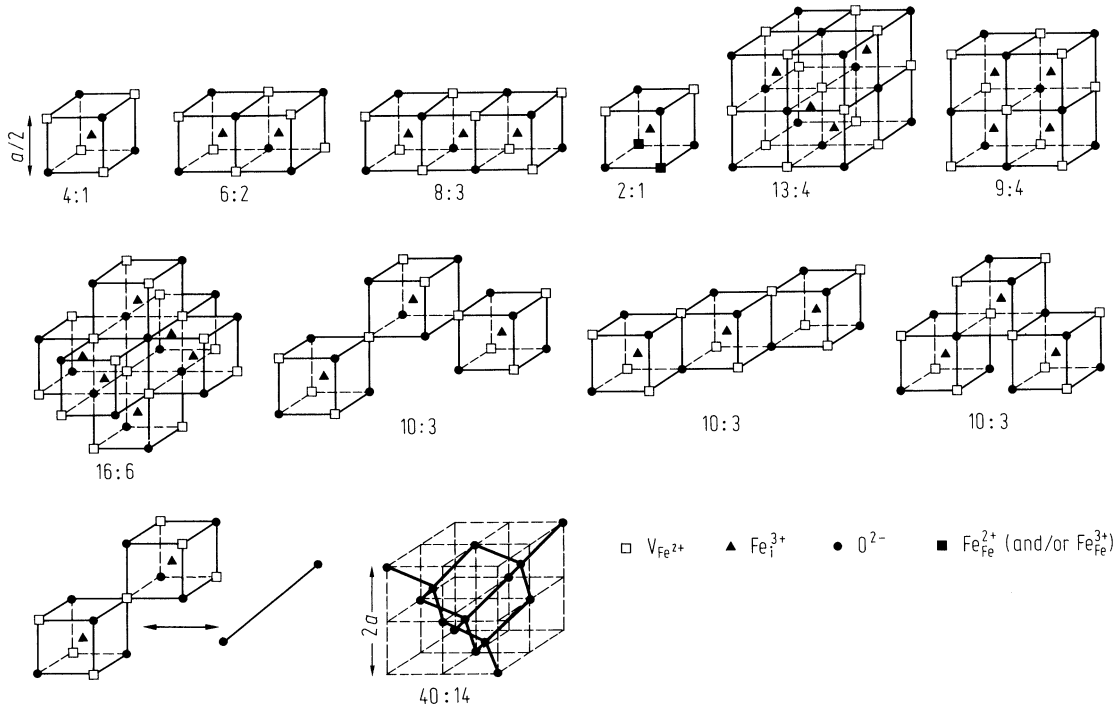

Fig. 2.

$Fe_{1-x}O$. 16:5 spinel-like aggregate [79G, 77C].

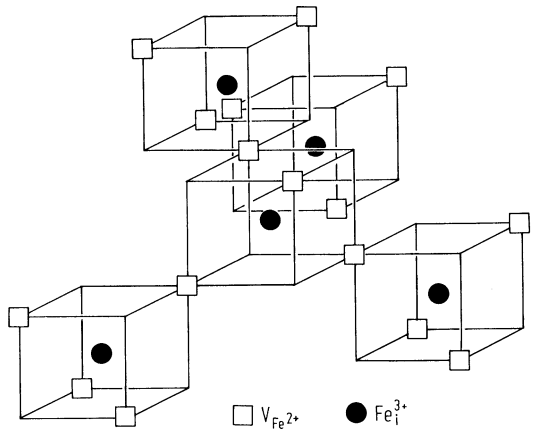

Fig. 3.

$Fe_{1-x}O$. Non-stoichiometry vs. oxygen partial pressure for different temperatures. The curves marked n = 4 and n = 6 are theoretical slopes $x \propto p_{O_2}^{1/n}$ [65V].