

Oxygen fugacity for stoichiometric magnetite Fe_3O_4 –hercinite FeAl_2O_4 solid solutions

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Abstract

The Frenkel defect model is applied to determine the oxygen fugacity that corresponds to the preparation of magnetite–hercinite solid solutions with an exact 4:3 oxygen:cation ratio. The results are presented in graphic form for $T = 1300^\circ\text{C}$.

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It is well known that the properties of many oxides depend critically on the oxygen stoichiometry. Among the best examples of this effect are V_2O_3 , where the temperature of the metal–insulator transition varies from 18 to 180 K, depending on the oxygen stoichiometry, and high T_C superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, that exhibit superconducting properties only over a small range of δ .

Another conspicuous example is magnetite Fe_3O_4 . This material, originally regarded as a model ionic compound, is now viewed as a much more complex system (see the extended discussion by Garcia [1]) in which the physical properties strongly depend on stoichiometry.

Twenty years ago a systematic investigation of the influence of oxygen stoichiometry on the physical properties of magnetite, in particular on the Verwey transition, was undertaken at Purdue University. The Verwey metal–insulator transition in magnetite is usually believed to originate from ionic ordering of the Fe ions at the octahedral sites [2] and is accompanied by abrupt changes in many physical characteristics, e.g., resistivity, specific heat, and elastic properties. The transition is also reflected in the change of the crystal

structure from high temperature cubic ($Fd\bar{3}m$) to the low temperature monoclinic (Cc) symmetry.

It was found that this phase transformation may be highly influenced by changing stoichiometry [3]: for example, the Verwey transition temperature T_V lowers from 120 K (stoichiometric Fe_3O_4) to 80 K for $\text{Fe}_{3(1-\delta)}\text{O}_4$, with $\delta = 0.039$, and at the critical vacancy concentration, $3\delta = 0.012$, the transition changes its character from first to higher order (or to the domain state, in which LRO no longer prevails [4]).

Later, the results on nonstoichiometry were complemented with systematic investigations of the effect of titanium [5] and zinc [6] substitution in magnetite. These nonmagnetic dopants were selected since they enter different lattice positions: octahedral substitutions occur in $\text{Fe}_{3-z}\text{Ti}_z\text{O}_4$ and tetrahedral, in $\text{Fe}_{3-z}\text{Zn}_z\text{O}_4$, thus providing a means for introducing an independent perturbation of the cations on different types of structural sites.

Even very small doping levels (below 1%), also with other elements [7], alter both the transition temperature (Fig. 1) and the nature of the transition in a manner similar to that caused by introduction of cation vacancies δ .

Therefore, proper sample preparation procedures are crucial to the reliability of the experimental results.

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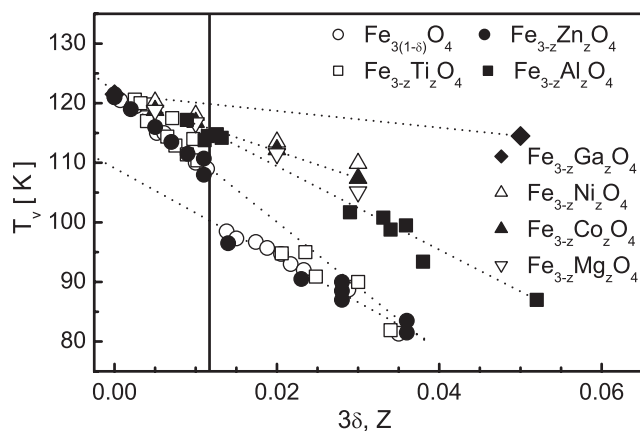


Fig. 1. Verwey temperature T_V dependence upon doping z and nonstoichiometry levels 3δ . Data for Ga, Ni, Co, Mg are taken from Rozenberg et al. [8]. The vertical solid line marks the critical concentration of Zn, Ti and nonstoichiometry level 3δ below which the Verwey transition is discontinuous; the dashed lines are guides-for-the-eye.

Also, other parameters, such as external pressure [8] or isotope substitution [9], shift the transition temperature. It is thus crucial to ensure that different factors causing the change of transition are not intermingled. At the very least, the oxygen stoichiometry must be well controlled.

This recognition prompted studies of point defect equilibria involved in Zn [10] and Ti [11] substitutions; these were subsequently used to ensure the stoichiometry of samples by the establishment of the proper conditions for annealing (oxygen fugacity vs. defect concentration).

The objective of this brief report is to expand on this discussion for the case of aluminum-doped ferrites (magnetite Fe_3O_4 —hercinite FeAl_2O_4 solid solution). This work complements our earlier studies of this material [12], where we also found that Al alters T_V (Fig. 1) and other physical properties of magnetite. Therefore, in this material as well, it is crucial to establish annealing conditions that will ensure the correct stoichiometry of specimens.

The discussion presented below follows closely the treatment of the same problem for titanomagnetites presented in [11].

The stability field of the Fe_3O_4 – FeAl_2O_4 system (shown after Meyers et al. [13] in Fig. 2 for $T = 1280^\circ\text{C}$ as dashed lines) represents the range of oxygen fugacities over which the single phase can exist.

Following [11] we assume that nonstoichiometry arises from cationic point defects of the Frenkel type and that it is associated with the magnetite component of the spinel only. That is, we assume the stability field of zero width for FeAl_2O_4 , which, although being approximate, can be adopted as a first approximation [11], especially in comparison with wide range of nonstoichiometry in Fe_3O_4 .

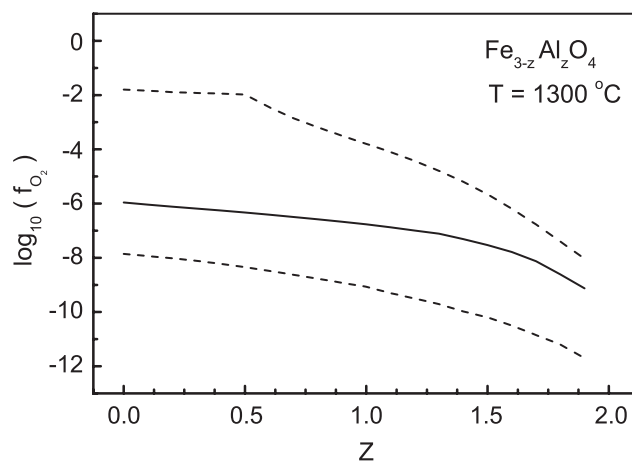


Fig. 2. The variation of $\log(f_{\text{O}_2})$ at 1300°C for stoichiometric magnetite–hercinite solid solution as a function of Al content (solid line—this work) and the stability field of the Fe_3O_4 – FeAl_2O_4 system (dashed lines—after Meyers et al. [13]).

The total number of moles of cations and defects (n_Σ) is defined as

$$n_\Sigma = n_{\text{Fe}^{3+}} + n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}} + n_V, \quad (1)$$

where n_M ($M = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}$) stands for the number of moles of cations, and n_V is the number of moles of vacancies. The number of interstitial iron ions n_I is already included in the iron cation sum.

The reaction between normally located iron ions, interstitials, and vacancies within the magnetite component may be represented by

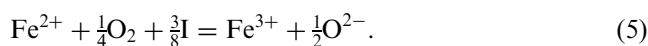
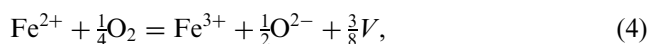


with an associated equilibrium constant [14]

$$K_1 = \frac{n_V n_I}{(n_\Sigma)^2}. \quad (3)$$

Deviations from ideality may be neglected because the defect concentration is very small.

In the oxidation reaction, every additional oxygen atom generates $\frac{3}{4}$ cationic sites or eliminates $\frac{3}{4}$ interstitial cations (which now can assume ‘normal’ positions), according to the formulas



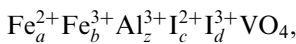
In addition, we assume that the oxidation reaction affects only the magnetite component of the spinel, i.e. only the $1 - z/2$ portion of the entire $(1 - z/2)\text{Fe}_3\text{O}_4 \cdot (z/2)\text{FeAl}_2\text{O}_4 = \text{Fe}_{3-z}\text{Al}_z\text{O}_4$ solid solution. Also, we treat the O^{2-} chemical potential as a constant. With these assumptions, according to the mass action law, appropriate equilibrium constants for Eqs. (4) and (5) are specified by

$$K_2 = \frac{n_{\text{Fe}^{3+}}}{n_{\text{Fe}^{2+}}} (f_{\text{O}_2})^{-1/4} \left(\frac{n_V}{(1 - \frac{z}{2})n_\Sigma} \right)^{3/8}, \quad (6)$$

$$K_3 = \frac{n_{\text{Fe}^{3+}}}{n_{\text{Fe}^{2+}}} (f_{\text{O}_2})^{-1/4} \left(\frac{n_{\Sigma}}{(1 - \frac{z}{2})n_1} \right)^{3/8}. \quad (7)$$

The reactions leading to these equations are related by Eq. (3), so either of them can be used in subsequent analysis; as both K_2 and K_1 constants are experimentally known, we will use Eq. (6).

Additionally, the number of cations and defects are subject to electroneutrality and mass constraints. Describing our system in terms of



the electroneutrality constraint now reads

$$2a + 3b + 3z + 2c + 3d = 8,$$

and for the conservation of mass condition,

$$3 - (a + b + z) = V,$$

where we explicitly counted interstitials of different valence.

The above two conditions lead subsequently to the equation

$$\frac{1}{8}(6a + 9b + 9z) + \frac{3}{8}(2c + 3d) = a + b + z + V,$$

which can be solved for the parameter $n_V - n_I$:

$$n_V - n_I = \frac{1}{8}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}}), \quad (8)$$

with $a + c \sim n_{\text{Fe}^{2+}}$, $b + d \sim n_{\text{Fe}^{3+}}$, $c + d \sim n_I$, $V \sim n_V$.

This parameter describes the level of nonstoichiometry in the system and is equal to zero for stoichiometric aluminum magnetite. Eq. (8) can be solved for n_V when n_I is introduced from Eq. (3):

$$n_V^2 - K_1 n_{\Sigma}^2 - \frac{1}{8}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}}) \cdot n_V = 0.$$

The solution for n_V now reads

$$2n_V = \frac{1}{8}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}}) + \sqrt{\frac{1}{64}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}})^2 + 4K_1 n_{\Sigma}^2}. \quad (9)$$

Then, from Eqs. (6) and (9) we obtain the expression

$$2n_V = \frac{1}{8}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}}) + \sqrt{\frac{1}{64}(n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}})^2 + 4K_1 n_{\Sigma}^2}, \quad (10)$$

for the equilibrium oxygen fugacity, which can then be evaluated for any degree of nonstoichiometry once the reaction constants K_1 and K_2 are known.

For stoichiometric samples ($n_{\text{Fe}^{3+}} - 2n_{\text{Fe}^{2+}} + n_{\text{Al}^{3+}} = 0$) Eq. (10) reduces to

$$f_{\text{O}_2}^{1/4} = \frac{1}{K_2} \frac{n_{\text{Fe}^{3+}}}{n_{\text{Fe}^{2+}}} \frac{K_1^{3/16}}{(1 - \frac{z}{2})^{3/8}}.$$

Substituting $2 - z$ for $n_{\text{Fe}^{3+}}/n_{\text{Fe}^{2+}}$ we finally get

$$f_{\text{O}_2}^{1/4} = 2 \frac{K_1^{3/16}}{K_2} \frac{2 - z}{2(1 - \frac{z}{2})^{3/8}}. \quad (11)$$

Introducing the intrinsic oxygen fugacity for stoichiometric magnetite, a value well known from the literature [14],

$$(f_{\text{O}_2}^{\text{Fe}_3\text{O}_4})^{1/4} = 2 \frac{K_1^{3/16}}{K_2},$$

we obtain the variation of $\log(f_{\text{O}_2})$ for the stoichiometric magnetite–hercinite solid solution as a function of Al content

$$\log(f_{\text{O}_2}) = \log(f_{\text{O}_2}^{\text{Fe}_3\text{O}_4}) + 2.5 \log\left(\frac{2 - z}{2}\right). \quad (12)$$

The formula (Eq. (12)) is the reasonable approximation at low aluminum concentration, although for the higher Al concentrations the assumptions adopted in the derivation of the above expression may no longer hold. The results of the above calculations at $T = 1300^\circ\text{C}$ are presented in Fig. 2 as a solid line. It is seen that the calculated curve fall roughly midway between the composition limits delineated by the dashed lines.

In conclusion, the relationship between composition of Al based ferrites for low Al concentration and intrinsic oxygen fugacity has been established, based on the Frenkel cation point defect model. These results should be useful to program annealing experiments designed to produce stoichiometric magnetite–hercinite solid solutions.

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