Hydrogen Reduction of Cu-Mn-Fe-O Spinel Solid Solutions

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Abstract—The crystal-chemical transformations accompanying the hydrogen reduction of $Cu_x Mn_{1-x} Fe_2O_4$ (x = 0.2, 0.5, 0.8) solid solutions are investigated, and general equations describing these processes over the entire composition range ($0 \le x \le 1$) are derived. The results on the character of the processes involved differ radically from earlier findings. The equilibrium oxygen pressure is evaluated for the low-oxygen phase boundsolid solutions throughout region. ary of the spinel their stability For $(MnFe_2O_4)_{x_1}(Cu_{0.5}Fe_{2.5}O_4)_{x_2}(CuFe_2O_4)_{1-x_1-x_2}$ solid solutions, which are of practical interest, the $\log p_{O_2}(1/T)$ data are well represented by the equation $\log (p_{O_2}/Pa) \pm 0.4 = 12.8 - 3.7x_1 - 2.8x_2 - 10280/T$, which is of importance in controlled synthesis of single-phase materials in this system.

INTRODUCTION

The presence of metals of variable valence in Cu– Mn–Fe–O spinel solid solutions and the Jahn–Teller nature of the Cu²⁺ and Mn³⁺ ions [1] may lead, under certain conditions, to complex redox processes and structural transformations in these materials, resulting in structure-sensitive properties of practical importance, in particular, square hysteresis loops [2]. Since these solid solutions are attractive electronic materials [3], the study of their formation and decomposition is of considerable interest. Such information is also important in the processing of polymetallic ores [4]. These issues, however, have not yet been studied in sufficient detail [5].

For example, only the initial steps of reduction processes have been investigated. Some of the reported data are in conflict with well-known laws of thermodynamics. No equations have been reported for the complete reduction of the solid solutions in question. Data on the synthesis and cooling conditions for singlephase samples are also missing.

This paper addresses the points raised above.

RESULTS AND DISCUSSION

The synthesis procedure and characterization techniques we used were described in detail elsewhere [6, 7].

Figure 1 shows the equilibrium oxygen pressure p_{O_2} and the lattice parameters of the spinel and wüstite phases as functions of the degree of reduction η for Cu_xMn_{1-x}Fe₂O₄ spinel solid solutions (x = 0.8, 0.5, 0.2) at 1270 K ($\eta = 100\%$ corresponds to the complete removal of oxygen from the solid solution).

Phase transitions and changes in the cation composition of solid solutions influence their $p_{O_2}(\eta)$ and $a(\eta)$ curves. The reduction process can be divided into six steps.

During the first step, p_{O_2} decreases, and a_{sp} rises (Fig. 1). According to x-ray diffraction (XRD) data, this step involves the formation of the rhombohedral phase CuFeO₂, which coexists with the spinel phase. Based on earlier results [8, 9], we conclude that these changes are associated with the reduction of CuFe₂O₄ and an increase in the content of Cu_{0.5}Fe_{2.5}O₄, which has larger *a* and lower p_{O_2} .

Therefore, the crystal-chemical transformations involved in the reduction of $Cu_xMn_{1-x}Fe_2O_4$ solid solutions (0 < *x* < 1) in this step can be represented by the scheme

$$Cu_{x}Mn_{1-x}Fe_{2}O_{4} + mH_{2}$$

= (1-m)[(CuFe_{2}O_{4})_{x-2m/(1-m)} (1)
× (Cu_{0.5}Fe_{2.5}O_{4})_{m/(1-m)}(MnFe_{2}O_{4})_{1-x/(1-m)}] (1)
+ 1.5mCuFeO_{2} + mH_{2}O.

At the end of this step, $CuFe_2O_4$ is fully reduced (all of the Cu^{2+} is reduced to Cu^+). It follows from (1) that, for x = 1, 0.8, 0.5, and 0.2, this occurs at m = 0.5, 0.4, 0.25, and 0.1, respectively, or at $\eta = 12.5, 10, 6.25$, and 2.5% ($m = \eta/25$). The corresponding compositions of the spinel phase are represented in Fig. 2 by points B ($Cu_{0.5}Fe_{2.5}O_4$), B₁ (($Cu_{0.5}Fe_{2.5}O_4$)_{2/3}(MnFe₂O₄)_{1/3}), B₂ (($Cu_{0.5}Fe_{2.5}O_4$)_{1/3}(MnFe₂O₄)_{2/3}), and B₃ (($Cu_{0.5}Fe_{2.5}O_4$)_{0.11}(MnFe₂O₄)_{0.89}). The associated changes in the composition of the spinel phase and



Fig. 1. (1, 1') Equilibrium oxygen pressure and lattice parameters of the wüstite (2, 2') and spinel (3, 3') phases vs. degree of reduction for $Cu_xMn_{1-x}Fe_2O_4$ solid solutions with x = (a) (1-3) 0.8, (1'-3') 0.2, and (b) 0.5 at 1270 K.

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Fig. 2. Equilibrium oxygen pressure vs. composition of the spinel phase for $Cu_x Mn_{1-x} Fe_2 O_4$ solid solutions reduced at 1270 K.

log p_{O_2} are represented in Fig. 2 by the A–B, A₁–B₁, A₂– B₂, A₃–B₃, A'–B', A'₁–B'₁, A'₂–B'₂, and A'₃–B'₃ lines in the (CuFe₂O₄)_{C₁}(Cu_{0.5}Fe_{2.5}O₄)_{C₂}(MnFe₂O₄)_{1–C₁-C₂} composition triangle. The data for x = 1 are taken from Zalazinskii *et al.* [8]. According to Shchepetkin *et al.* [10], the composition dependence of the lattice parameter for the solid solutions in question follows the additivity rule,

$$a(\text{\AA}) = 8.389C_1 + 8.414C_2 + 8.511(1 - C_1 - C_2), (2)$$

where C_1 and C_2 are the mole fractions of $CuFe_2O_4$ and $Cu_{0.5}Fe_{2.5}O_4$, respectively.

The composition dependences of the lattice parameter calculated by Eq. (2) for the A_1-B_1 , A_2-B_2 , and A_3-B_3 cuts coincide with experimental data to within the measurement accuracy,¹ which lends support to the proposed mechanism, represented by scheme (1).

In the second step of reduction, the phase composition remains unchanged, but the dependences of a on η , p_{O_2} on η , and p_{O_2} on composition change sharply because of the qualitative changes in the composition of the spinel phase: magnetite (Fe₃O₄) replaces CuFe₂O₄ (Fe²⁺ instead of Cu²⁺). The composition of the spinel phase varies within the (Cu_{0.5}Fe_{2.5}O₄)_{C₂}(Fe₃O₄)_{C₃}(MnFe₂O₄)_{1-C₂-C₃ compo-}

¹ Given that $m = \eta/25$ and that, according to (1), the composition of the solid solution depends on *m* at a given value of *x*, the composition dependence of *a* can be converted easily to $a(\eta)$ (Fig. 1) and vice versa.

sition triangle. The content of $Cu_{0.5}Fe_{2.5}O_4$ decreases, and those of Fe_3O_4 and $CuFeO_2$ increase, as represented by the scheme

$$Cu_{x}Mn_{1-x}Fe_{2}O_{4} + mH_{2}$$

= (1-m)[(Cu_{0.5}Fe_{2.5}O_{4})_{2x-3m/(1-m)})
× (MnFe_{2}O_{4})_{1-x/(1-m)}(Fe_{3}O_{4})_{2m-x/(1-m)}] (3)

+
$$1.5m$$
CuFeO₂ + m H₂O.

At the end of the second step, p_{O_2} ceases to decrease (Fig. 1). At x = 1, 0.8, 0.5, and 0.2, this step terminates at $\eta = 15.7, 12.2, 7.6, and 3\%$, respectively. According to scheme (3), the corresponding compositions are $Cu_{0.15}Fe_{2.85}O_4$ (C), $(Cu_{0.5}Fe_{2.5}O_4)_{0.276}(MnFe_2O_4)_{0.389}$. $(Fe_3O_4)_{0.335}$ (C₁), $(Cu_{0.5}Fe_{2.5}O_4)_{0.126}(MnFe_2O_4)_{0.719}$. $(Fe_3O_4)_{0.155}$ (C₂), and $(Cu_{0.5}Fe_{2.5}O_4)_{0.045}(MnFe_2O_4)_{0.91}$. $(Fe_3O_4)_{0.045}$ (C₃) (Fig. 2).

This mechanism of crystal-chemical transformations in the second step is supported by the fact that the $a(\eta)$ curves displayed in Fig. 1 coincide to within the experimental accuracy with those calculated using scheme (3) and the equation [10]

$$a(\text{\AA}) = 8.414C_2 + 8.395C_3 + 8.511(1 - C_2 - C_3), (4)$$

where C_2 and C_3 are the mole fractions of $Cu_{0.5}Fe_{2.5}O_4$ and Fe_3O_4 , respectively.

In the third step, the $CuFeO_2$ compound is reduced to copper metal and a spinel phase of composition $Cu_{0.15}Fe_{2.85}O_4$ [11] according to the scheme

$$ACuFeO_{2} + \Delta mH_{2} = (A - 1.68\Delta m)CuFeO_{2} + 0.59\Delta mCu_{0.15}Fe_{2.85}O_{4} + 1.59\Delta mCu + \Delta mH_{2}O,$$
(5)

where A is the amount of $CuFeO_2$ at the end of the second step, which can be found using scheme (3). At the end of the third step, all of the CuFeO₂ is reduced, i.e., $A - 1.68\Delta m = 0$ and $\Delta m = A/1.68$. Given that $\Delta \eta =$ $25\Delta m$, we obtain that at the end of the third step $\eta =$ $\eta_2 + 25\Delta m$, where η_2 is the degree of reduction at the end of the second step. Since p_{O_2} is constant, the composition of the spinel phase may only vary during reduction along a line of constant p_{O_2} (isobar), equal to p_{O_2} for CuFeO₂ and Cu_{0.15}Fe_{2.85}O₄, i.e., the $\log(p_{0}/Pa) = -1.7$ (an average of the data reported in [12] and displayed in Fig. 1). In Fig. 2, this line is labeled $C-C_3$. It passes through the representative points C, C₁, C₂, and C₃ of the solid solutions corresponding to the beginning of the third step, which dissolve $Cu_{0.15}Fe_{2.85}O_4$ during the reduction of CuFeO₂. Their compositions vary along an isobar in the ranges C_1-D_1 (x = 0.8), C_2-D_2 (x = 0.5), and C_3-D_3 (x = 0.2).²

For example, it follows from scheme (3) that, at x = 0.5, the amount of CuFeO₂ at the end of the second step is 0.456 mol. The complete reduction of this phase according to scheme (5) yields $0.16Cu_{0.15}Fe_{2.85}O_4$. Dissolution of the latter phase in the spinel of composition C_2 leads to the formation of a spinel phase of composition (Cu_{0.5}Fe_{2.5}O₄)_{0.159}(MnFe₂O₄)_{0.584}(Fe₃O₄)_{0.257} (D₂) at the end of the third step ($\Delta m = 0.271$, $\eta_2 = 7.6\%$, $\eta =$ 14.3%). At x = 0.8 and 0.2, η at the end of this step is 23 and 5.75%, respectively. The corresponding compositions are (Cu_{0.5}Fe_{2.5}O₄)_{0.284}(MnFe₂O₄)_{0.260}(Fe₃O₄)_{0.456} (D₁) and (Cu_{0.5}Fe_{2.5}O₄)_{0.062}(MnFe₂O₄)_{0.849}(Fe₃O₄)_{0.089} (D₃) (Fig. 2).

The lattice parameter of the spinel phase decreases in the third step of reduction (Fig. 1) owing to the decrease in the content of $MnFe_2O_4$, the component with the largest *a*. The *a* values calculated for the third step agree well with experimental data.

Note that the reduction of CuFeO₂ to Cu and Fe₃O₄ assumed by Shchepetkin et al. [5] is thermodynamically implausible since at 273 K CuFeO₂ has $\log(p_{0}/Pa) = -(1.6-1.8)$ (see Fig. 1 and [12]), while Fe₃O₄ has $\log(p_{O_2}/Pa) = -7.8$ (see Fig. 2 and [7, 13]). Moreover, according to Shchepetkin et al. [5] the equilibrium phase at the beginning of the reduction of CuFeO₂ at constant p_{O_2} is $(Cu_{0.5}Fe_{2.5}O_4)_z(MnFe_2O_4)_{1-z}$ with z from 0.11 to 0.67. Actually, the p_{0_2} of these solid solutions depends on composition and differs from that of $CuFeO_2$ by two to three orders of magnitude (Fig. 2, lines $B'-B'_3$, $C'-C'_3$). According to Shchepetkin *et al.* [5], during the reduction of $CuFeO_2$ these solid solutions become richer in Fe₃O₄, which has an even lower $p_{0,2}$. This would lead to further strong changes in equilibrium $p_{O_{\gamma}}$ (Fig. 2), in conflict with the thermodynamics of the reduction of phases of constant composition ($p_{O_2} = \text{const}$).

In the fourth step of reduction, copper coexists with a spinel phase, and both p_{O_2} and *a* decrease (Fig. 1) owing to the reduction of the residual Cu_{0.5}Fe_{2.5}O₄:

$$Cu_{x}Mn_{1-x}Fe_{2}O_{4} + mH_{2}$$

= (1 - 0.25m)[(Cu_{0.5}Fe_{2.5}O_{4})_{2x-1.5m/(1-0.25m)})
× (MnFe_{2}O_{4})_{1-x/(1-0.25m)}(Fe_{3}O_{4})_{1.25m-x/(1-0.25m)}] (6)

 $+(x-0.75m)Cu + mH_2O.$

² At x = 1, the composition of the spinel phase remains unchanged (C = Cu_{0.15}Fe_{2.85}O₄), but its content increases.



Fig. 3. Composition dependence of the lattice parameter for $Mn_yFe_{1-y}O$ solid solutions in equilibrium with a spinel phase at 1270 K.

The compositions of the spinel phases with x = 1.0, 0.8, 0.5, and 0.2 vary along the C–E, D₁–E₁, D₂–E₂, and D₃–E₃ lines, respectively, and $\log p_{O_2}$ varies along the C'–E', D'₁–E'₁, D'₂–E'₂, and D'₃–E'₃ lines (Fig. 2). At the end of this step, Cu_{0.5}Fe_{2.5}O₄ is fully reduced. It follows from scheme (6) that this occurs at $\eta = 33.3\%$ for x = 1.0, 26.7% for x = 0.8, 16.7% for x = 0.5, and 6.7% for x = 0.2. The corresponding compositions are Fe₃O₄ (E), (MnFe₂O₄)_{0.273}(Fe₃O₄)_{0.727} (E₁), (MnFe₂O₄)_{0.6}(Fe₃O₄)_{0.4} (E₂), and (MnFe₂O₄)_{0.857}(Fe₃O₄)_{0.143} (E₃).

The lattice parameters calculated using Eqs. (4) and (5) agree with experimental data to within the measurement accuracy.

In the fifth step, copper is in equilibrium with spinel and wüstite phases of variable composition. In the course of reduction, p_{O_2} decreases steadily, as do a_{sp} and a_w , attesting to a decrease in the concentrations of MnFe₂O₄ and MnO, respectively, which have smaller lattice parameters compared to Fe₃O₄ and FeO. Near the end of this step, the percentage of the spinel phase decreases, and p_{O_2} and a_{sp} approach those of Fe₃O₄. Finally, the spinel phase disappears, and the percentage of the wüstite phase reaches a maximum. The crystalchemical transformations involved in the reduction of Cu_xMn_{1-x}Fe₂O₄ solid solutions (0 < x < 1) can be represented by the scheme

$$Cu_{x}Mn_{1-x}Fe_{2}O_{4} + mH_{2}$$

$$= (1 + x - m)[(MnFe_{2}O_{4})_{(1-x)-(3m-4x)y/(1+x-m)} (7)$$

$$\times (Fe_{3}O_{4})_{1-[(1-x)-(3m-4x)y/(1+x-m)]}]$$

$$+ (3m - 4x)Mn_{y}Fe_{1-y}O + xCu + mH_{2}O.$$

At the end of this step, 1 + x - m = 0, i.e., m = 1 + x. This occurs at m = 2 ($\eta = 50\%$), 1.8 ($\eta = 45\%$), 1.5 ($\eta = 37.5\%$), 1.2 ($\eta = 30\%$), and 1 ($\eta = 25\%$) for x = 1, 0.8, 0.5, 0.2, and 0, respectively.

As seen from scheme (7), the composition of the spinel phase depends on that of the wüstite phase $Mn_yFe_{1-y}O$. The latter can be evaluated from the lattice parameter a_w (Fig. 1) using the plot of a_w versus y in Fig. 3, which is well represented by the best fit equation

$$a_{\rm w} = 4.3 + 0.143y. \tag{8}$$

Using the plot in Fig. 1 to evaluate a_w for a given value of η (within the step in question), one can then determine *y* (the composition of the wüstite phase) from Eq. (8). Next, substituting *y* in (7), one can find the composition of the spinel phase corresponding to the preset η . Comparison of the experimentally determined lattice parameter (Fig. 1) with the *a* calculated by Eq. (4) allows one to assess the accuracy of this procedure. The data for the *x* = 0.5 solid solution (Table 1)

Table 1. Composition and lattice parameter of the spinel phase and composition of the wüstite phase in $Cu_{0.5}Mn_{0.5}Fe_2O_4$ during the fifth step of reduction ($\eta = 16.7-37.5\%$)

| η, % | Wüstite phase | Spinel phase | $a_{ m sp}^{ m meas}$, Å | $a_{\rm sp}^{\rm calc}$, Å [Eq. (4)] |
|------|---|--|---------------------------|---------------------------------------|
| 16.7 | _ | $(MnFe_2O_4)_{0.6}(Fe_3O_4)_{0.4}$ | 8.463 | 8.465 |
| 20.0 | Mn _{0.289} Fe _{0.711} O | $(MnFe_2O_4)_{0.549}(Fe_3O_4)_{0.451}$ | 8.460 | 8.459 |
| 27.5 | Mn _{0.266} Fe _{0.734} O | $(MnFe_2O_4)_{0.388}(Fe_3O_4)_{0.612}$ | 8.438 | 8.436 |
| 35.0 | Mn _{0.224} Fe _{0.776} O | $(MnFe_2O_4)_{0.08}(Fe_3O_4)_{0.92}$ | 8.403 | 8.405 |
| 37.5 | $Mn_{0.2}Fe_{0.8}O$ | _ | _ | _ |

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validate this approach and lend support to the mechanism represented by scheme (7).³

In the sixth step, a wüstite phase of variable composition is in equilibrium with Cu and Fe, p_{O_2} decreases, and a_w rises. The changes in p_{O_2} and a_w are related to the decrease in the content of FeO, which has a higher equilibrium oxygen pressure and smaller lattice parameter in comparison with MnO. In this step, the FeO in Mn_yFe_{1-y}O is reduced to Fe metal according to the scheme⁴

$$Cu_{x}Mn_{1-x}Fe_{2}O_{4} + mH_{2}$$

= $(4-m)Mn_{(1-x)/(4-m)}Fe_{1-(1-x)/(4-m)}O$ (9)
+ $(m-x-1)Fe + xCu + mH_{2}O.$

This scheme is supported by the fact that the experimentally determined values of a_w (Fig. 1) agree with the a_w calculated by Eq. (8) for the wüstite solid solutions with the compositions obtained from (9) for preset η values.

At the end of the sixth step, all of the FeO is reduced to Fe, i.e., m - x - 1 = 2. This occurs at m = 4 ($\eta = 100\%$), 3.8 ($\eta = 95\%$), 3.5 ($\eta = 87.5\%$), 3.2 ($\eta = 80\%$), and 3 ($\eta = 75\%$) for x = 1, 0.8, 0.5, 0.2, and 0, respectively. Hydrogen does not reduce MnO. For this reason, after the sixth step, Fe and Cu are in equilibrium with MnO. The solid solution with x = 1 contains no MnO, and that with x = 0 contains no Cu, which also follows from scheme (9).

Thus, the proposed reaction schemes make it possible to quantify the crystal-chemical transformations involved in the reduction of $CuFe_2O_4$, $MnFe_2O_4$, and their solid solutions.

It follows from the data in Fig. 2 that, to obtain single-phase CuFe₂O₄–MnFe₂O₄–Fe₃O₄ solid solutions, one must know p_{O_2} as a function of temperature for each composition. Such data are presented in Fig. 4 for the low-oxygen phase boundary of some (MnFe₂O₄)_{x1}(Cu_{0.5}Fe_{2.5}O₄)_{x2}(Fe₃O₄)_{1-x1-x2} solid solutions (A) of practical importance [3, 14].

It is of interest to derive a general expression for $p_{O_2}(T)$ applicable to any solid solution in the system



Fig. 4. Plots of $\log p_{O_2}$ vs. inverse temperature for solid solutions in equilibrium with (*I*–5) CuFeO₂ and (6) Mn_yFe_{1-y}O [13]: (*I*) CuFe₂O₄, (2) Cu_{0.8}Mn_{0.2}Fe₂O₄, (3) Cu_{0.5}Mn_{0.5}Fe₂O₄, (4) (CuFe₂O₄)_{0.3}(Cu_{0.5}Fe_{2.5}O₄)_{0.3}(MnFe₂O₄)_{0.4}, (5) Cu_{0.2}Mn_{0.8}Fe₂O₄, (6) MnFe₂O₄.

under consideration. Using the data in Fig. 4 and the well-known formula [13]

$$\overline{\Delta H_0} \text{ (kJ/g-at)}$$

$$= 19.154 \times 10^{-3} \partial \log^{1/2} p_{\text{O}_2} / \partial (1/T), \qquad (10)$$

we calculated the partial solution enthalpy of oxygen (Table 2). The results demonstrate that the $\overline{\Delta H_0}$ of the Cu-containing solutions (A) with $x_1 \leq 0.8$ varies little

Table 2. Composition dependence of $\Delta \overline{H}_0$

| Composition | $-\Delta \overline{H}_0$, kJ/g-at |
|---|------------------------------------|
| CuFe ₂ O ₄ | 90.0 |
| $Cu_{0.8}Mn_{0.2}Fe_2O_4$ | 97.1 |
| $Cu_{0.5}Mn_{0.5}Fe_2O_4$ | 104.7 |
| $(CuFe_2O_4)_{0.3}(Cu_{0.5}Fe_{2.5}O_4)_{0.3}(MnFe_2O_4)_{0.4}$ | 104.3 |
| $Cu_{0.2}Mn_{0.8}Fe_2O_4$ | 106.3 |
| MnFe ₂ O ₄ | 308.2 |

Note: $\Delta \overline{H}_0$ averaged over the Cu-containing compositions is -98.4 ± 8.4 kJ/g-at.

³ The same refers to the other solid solutions.

⁴ As in the reaction schemes above, the possible variations in oxygen stoichiometry are here left out of consideration because they are relatively small and cannot influence the character of the crystal-chemical transformations under discussion.

with composition. In view of this, $\log p_{O_2}(1/T)$ can be expressed through the average of $\overline{\Delta H_0}$, equal to -98.4 kJ/g-at:

$$\log p_{\rm O_2} = B - 10280/T, \tag{11}$$

where *B* depends on composition. It follows from the data in Fig. 4 that, for solutions A with $x_1 \le 0.8$, $\log p_{O_2}$ varies almost linearly with composition. The 1270-K data are well represented by

$$\log(p_{0}/Pa) \pm 0.3 = x_1 + 1.9x_2 + 4.7(1 - x_1 - x_2).$$
 (12)

Substituting this relation in (11), we obtain

$$B = 12.8 - 3.7x_1 - 2.8x_2. \tag{13}$$

Combining Eqs. (11) and (13), we find $\log p_{O_2}$ as a function of composition and temperature for solutions A with $x_1 \le 0.8$:

$$\log(p_{O_2}/Pa) \pm 0.4$$

= 12.8 - 3.7 x₁ - 2.8 x₂ - 10280/T. (14)

Relation (14) is of theoretical and practical interest because it allows one to find, using simple calculations, the equilibrium oxygen pressure at the low-oxygen phase boundary of $(MnFe_2O_4)_{x_1}(Cu_{0.5}Fe_{2.5}O_4)_{x_2}(CuFe_2O_4)_{1-x_1-x_2}$ solid solutions in broad composition and temperature ranges, which is vital for controlled synthesis of single-phase materials in this system.

CONCLUSIONS

Hydrogen reduction of $Cu_xMn_{1-x}Fe_2O_4$ solid solutions occurs in six steps and involves the following consecutive changes in the oxidation states of Cu and Fe: $Cu^{2+} \rightarrow Cu^+$, $Fe^{3+} \rightarrow Fe^{2+}$, $Cu^+ \rightarrow Cu^0$, and $Fe^{2+} \rightarrow Fe^0$. The final reduction products are Cu, Fe, and MnO. The oxide with x = 1 contains no MnO, and that with x = 0 contains no Cu. The observed crystal-chemical transformations are well described by the proposed reactions schemes.

The reduction of CuFeO₂ yields Cu and Cu_{0.15}Fe_{2.85}O₄, rather than Cu and Fe₃O₄ as was reported earlier. As a result, the Cu content of the spinel phase increases again, and oxygen is released at constant p_{O_2} .

The equilibrium oxygen pressure varies widely with composition and temperature. In view of this, phase-

pure spinel solid solutions can only be prepared at controlled p_{O_2} .

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