The Formation of the Oxidized Fe_3O_4-Fe_2TiO_4 Solid Solution by the Air Oxidation of the Aqueous Suspension

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The oxidized Fe_3O_4-Fe_2TiO_4 solid solution with the spinel type structure was synthesized by means of ferrite methods at pH 9.0 and 65 °C. When the solid solution thus obtained was heated at 200 or 300 °C in air for 20 h, it was completely oxidized to form a ferromagnetic product, which retained the spinel type structure for Ti/Fe_{total} ratios from 0 to 0.5.

Akashi *et al.*[1] proposed a "Ferrite Method" to eliminate many kinds of heavy metal ions in waste waters with concentrations as high as 1000 ppm. It should be emphasized that the ferromagnetic sludges thus formed are completely separated from solutions by a magnet. Katsura *et al.*[2] have examined this method for treating concentrated laboratory waste waters, and have succeeded in establishing a station for eliminating the harmful heavy metal ions. Of course, the background of the ferrite method is greatly indebted to many previous fundamental studies of the formation of Fe_3O_4 by the air oxidation of a ferrous hydroxide suspension in slightly alkaline solution. During these investigations, Kiyama[3] established the stability field for the formation of Fe_3O_4 with respect to the temperature and alkalinity of the aqueous suspensions. Yasuoka *et al.*,[4] Hamamura *et al.*,[5] and Kiyama[6,7] have synthesized $MnFe_2O_4$, $ZnFe_2O_4$, $BaFe_2O_4$, and Mn- and Co-ferrites, respectively. Katsura *et al.*[2] and Kaneko and Katsura[8] have also studied the formation of a solid solution of $FeCr_2O_4$–Fe_3O_4 and the $MgFe_2O_4$–Fe_3O_4 solid solution by the ferrite method, respectively. Tamaura *et al.*[9] have studied the formation of Fe_3O_4 in the presence of a dispersing reagent. The formations of solid solutions between Fe_3O_4 and the double oxides are of much interest not only for the ferrite method, but also for the fundamental studies.

The presnet objectives are to: (1) ascertain whether or not a Fe_3O_4–Fe_2TiO_4 solid solution having the spinel type structure could be formed in its complete composition range by the ferrite method, and to (2) obtain a strongly oxidized Fe_2O_3–Fe_2TiO_5 solid solution having the ferromagnetic spinel type structure by heating the samples synthesized by the ferrite method at some higher temperatures. The latter objective is especially valuable for studying the magnetic or geomagnetic properties of highly oxidized titanomagneite found in igneous rocks.

Experimental

Reagents. The guaranteed reagent grade of $FeSO_4 \cdot 7H_2O$ and the reagent grade of $Ti(SO_4)_2 \cdot nH_2O$ were employed for preparing solutions with various Ti/Fe_{total} ratios ranging from 0 to 0.5.

Chemical Analysis. To determine Ti content in the reagent $Ti(SO_4)_2 \cdot nH_2O$ and the Ti^{4+}, Fe^{2+}, and Fe^{3+} contents in the ferrites obtained, the improved method of Iwasaki *et al.*[10] was used. But the ferrites containing various amounts of Ti^{4+} were easily dissolved by the 4 mol dm^{-3} sulfuric acid solution. Thus, there was no need to use the mixed acid solution of sulfuric acid and hydrofluoric acid.

Apparatus. The reaction vessel was a beaker with a capacity of 1 dm^3, as shown in Fig. 1. The temperature of the vessel was kept constant to 65±0.5 °C by a mantle heater controlled by an electric temperature controller. A glass tube (8) with a flat end having eight holes (0.1 cm in diameter) at equal intervals is kept in contact with the bottom of the beaker. A platinum electrode, and a calomel elctrode with a double junction are 1, 5, and 6 in Fig. 1. A thermister to control the temperature is 3 in Fig. 1, and 4 is a condenser.

Procedures. Re-distilled water (800 cm^3) was added to a separable beaker, and was flushed, using nitrogen gas free from carbon dioxide and oxygen for about 1 h. After the separable beaker was sealed, the solution was heated at 65±0.5 °C while the nitrogen gas bubbling was continued. $FeSO_4 \cdot 7H_2O$ (14.4 g) and a desired amount of the titanium(IV) sulfate solution were then added still continuing the flow of the nitrogen gas. Then, a 2 mol dm^{-3} sodium hydroxide solution free from carbon dioxide was added; the pH-stat controller was used to adjust the pH value at 9.0 or any desired value. After the solution stood for about 1 h, the pH value and the oxidation potential (ORP) became constant without further addition of the

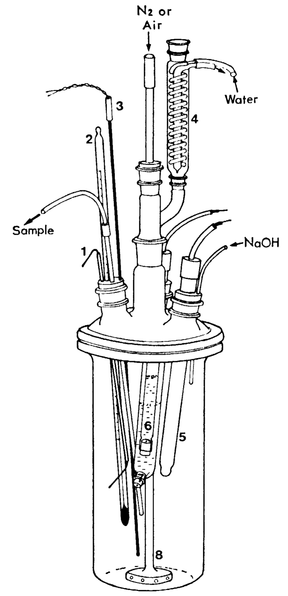

Fig. 1. The reaction vessel used in this study. The reaction vessel is separable. 1: Platinum electrode, 2: thermometer, 3: thermister, 4: condenser, 5: glass electrode, 6: calomel electrode with double junction 7, 8: glass tube with a flat end having eight holes (0.1 cm in diameter).

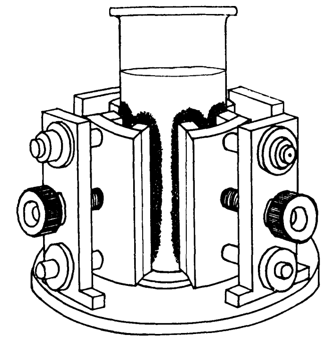

Fig. 2. Magnetic separator used in this experiment. The product is attracted by the four magnets with 1600 Oe and separated from the solution within 2—5 min.

2 mol dm^{-3} sodium hydroxide solution. Then, pre-purified air free from carbon dioxide was passed at a rate of 3 dm^3 min^{-1} through the solution in place of the nitrogen gas for a desired period of time. The temperature and the pH were kept constant during the course of the air oxidation. The end of the oxidation which completed the formation of the ferromagnetic spinel type product was easily recognized by mean of an oxidation potential measurement, as pointed out in previous studies.[8] The relationship between the ORP value and the Fe^{2+}/Fe_{total} ratio will be seen later. The oxidation product was separated from the solution in the nitrogen atmosphere by a magnetic separator devised specially for the present experiment. The magnetic separator used is illustrated in Fig. 2. The product attracted by the magnet was then washed with redistilled water several times, then with acetone to remove the water in the precipitate as completely as possible. The precipitate thus obtained was dried by the freeze-dry technique. The product was analyzed chemically to determine the contents of Fe^{2+}, Fe^{3+}, and Ti^{4+}. The dried product was examined by the powder X-ray diffraction method, infrared spectroscopy, and electron microscopy to identify the phases present in the product. The 2θ angles of the diffraction peaks were calibrated against the standard Si powder by using the Mn-filtered Fe $K\alpha$ radiation. The magnetic susceptibility and the Mössbauer spectra were also obtained for extremely oxidized Fe_2O_3-Fe_2TiO_5 solid solution having the spinel type structure. The results obtained from these magnetic and Mössbauer studies will be publised in the near future.

In order to determine the oxidation rate in the aqueous suspension, an aliquot portion of the suspended solution containing oxide and/or hydroxide was taken out by a syringe in the course of the air oxidation, as seen in Fig. 1, without any air contamination.

Results and Discussion

(1) *The Hydrolysis of Titanium in the Presence of the* Fe^{2+} *Ion in Aqueous Suspension.* Kaneko and Katsura[8] pointed out that the process of hydrolysis is important for producing the ferrite solid solution. In this paper, the acidic solution containing titanium(IV) and iron(II) ions (Ti/Fe ratio of 0.304) was titrated with a 2 mol dm^{-3} sodium hydroxide solution. The result is shown in Fig. 3. As seen here, the titanium(IV) ions were almost completely hydrolyzed at about pH 9. So, at pH 9.0, all ions of titanium(IV) and iron(II) were in the hydrous state. This suggests that the complete solid solution of Fe_2TiO_4-Fe_3O_4 could be produced by the ferrite method at a pH of 9.0 and at 65 °C, provided that the hydrolysis is one of the definite steps needed to form the ferrite, as pointed out in the previous paper.[8]

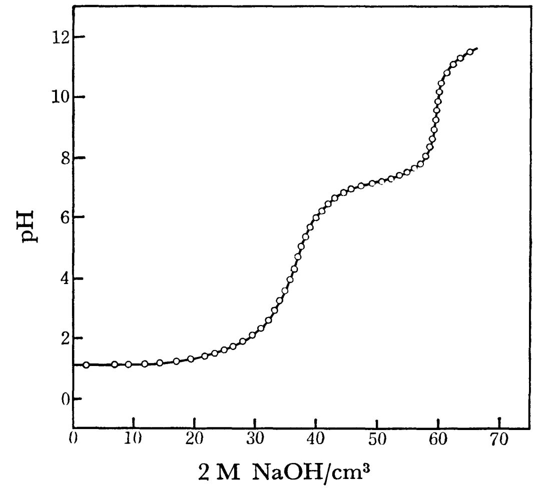

Fig. 3. The titration curve for Ti^{4+} and Fe^{2+}. The Ti/Fe_{total} ratio is 0.304, and the concentration of the NaOH solution is 2 M.

(2) *The Oxidation Rate to Form the* Fe_3O_4*-*Fe_2TiO_4 *Solid Solution.* Figure 4 shows the relationship between the Fe^{2+}/Fe_{total} ratio in the suspended solution and the reaction time(min) in the case of the ferrous hydroxide alone($Ti/Fe_{total}=0$). The measurements were performed at pH 9.0 and 11.0 at 65 °C. The ORP dependence of the Fe^{2+}/Fe_{total} ratio is also plotted in Fig. 4. As seen here, the ORP values changed abruptly from about −800 to −50 mV at pH values 9.0 and 11.0, as pointed by the letters a and b. In the early stage of the oxidation, which ranged from

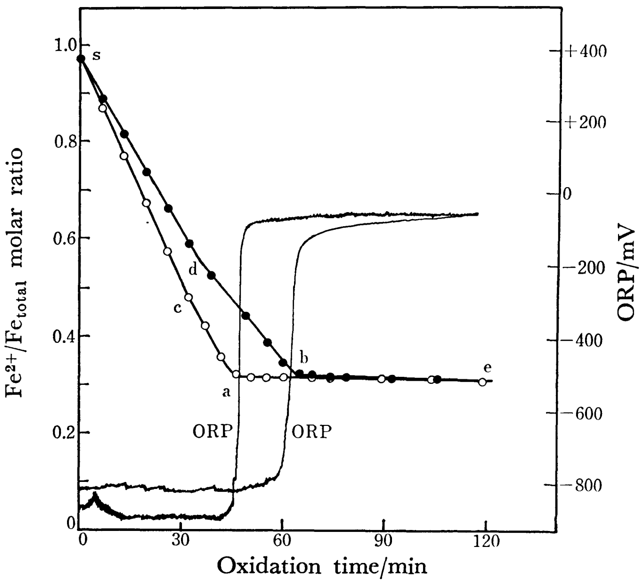

Fig. 4. The oxidation rate of the $Fe(OH)_2$ suspension by the air and the change of the oxidation potential (Pt-Calomel couple). The Ti/Fe_{total} molar ratio is 0.

point s to a or b, as is clear in Fig. 4, the oxidation rate was high, and the rate seems to be a zero order reaction. However, considering the present accuracy of chemical analysis, we may say that the oxidation rate in the early stage is constructed by two somewhat different straight lines; one is from s to d the other is from d to b at pH 9.0, and from s to c and c to a at pH 11.0. According to the results of the X-ray diffraction method and the electron microscopy, there was a large amount of ferrous hydroxide in the suspensions produced during the course from s to c or d, then gradually the amount of ferrous hydroxdie was decreased to form a large amount of ferrite in the course from d or c to b or a. At point a or b, no ferrous hydroxide crystals were found in the suspension. The oxidation rate changed greatly at just the same point as where the ORP value changed abruptly by a or b in Fig. 4. The electrochemical discussion on this phenomenon will be presented in the near future.

Figures 5 and 6 show the same relationship between the Fe^{2+}/Fe_{total} ratio in the suspended solution and the reaction time in cases of the Ti/Fe_{total} ratios of 0.071 and 0.304, respectively. As seen in Figs. 5 and 6, the great changes in the ORP values correspond to the end points of the oxidation reaction for producing the ferrite containing titanium. Because of these results, the oxidation by the air was stopped just 10 min after the abrupt change of the ORP value, and the ferromagnetic suspension was separated and dried as described before. We call the dried product thus obtained series A.

(3) *The Non-stoichiometry in Composition.* As seen in Figs. 4, 5, and 6, the compositions of the series A are not stoichiometric and the deviation from the stoichiometric composition increases with increasing the Ti/Fe_{total} ratio. For example, in the case of the Ti/Fe_{total} ratio of 0.304, the Fe^{2+}/Fe_{total} ratio should be 0.739 if the composition is stoichiometric, but as seen in Fig. 6, the real ratio was only 0.290. This means that the series A is oxidized. The X-ray diffraction pattern of each product showd only a typical spinel type structure.

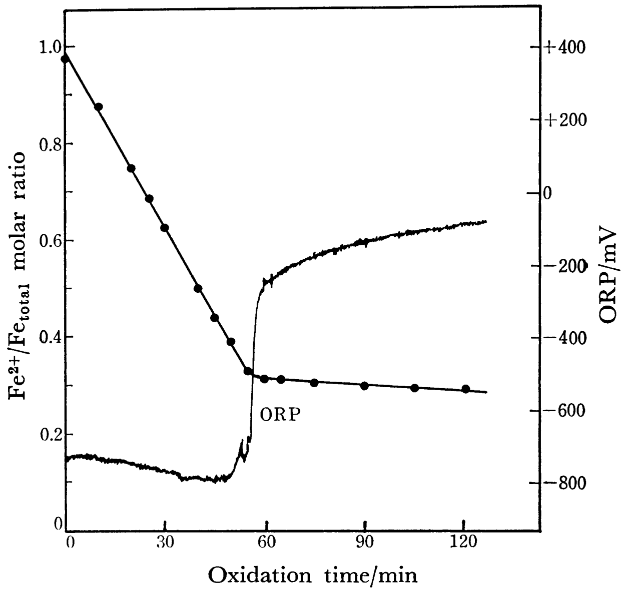

Fig. 5. The oxidation rate of the suspension by the air (Pt-Calomel couple). The Ti/Fe_{total} molar ratio is 0.071.

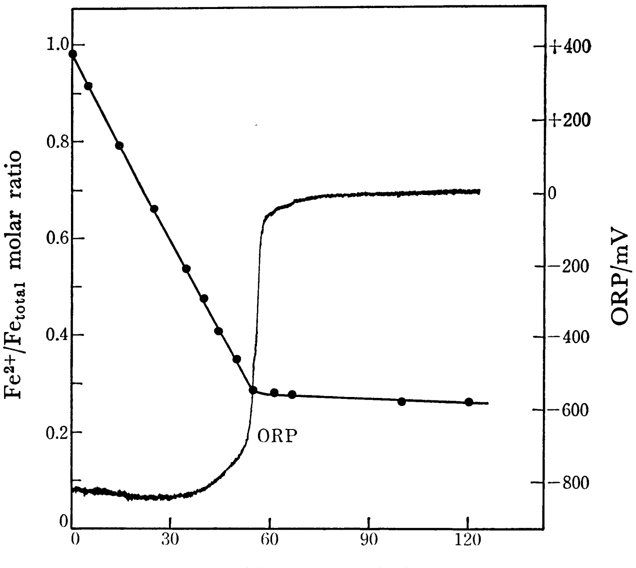

Fig. 6. The oxidation rate of the suspension by the air (Pt-Calomel couple). The Ti/Fe_{total} molar ratio is 0.304.

(4) *Synthesis of the Extremely Oxidized Fe_2TiO_4–Fe_3O_4 Solid Solution.* The series A was subsequently heated at a temperature range from 80 to 400 °C in air by an electrical furnace for desired periods of time. The product thus obtained is called the series B. The series B was examined by the X-ray diffraction method, infrared spectroscopy, electron microscopy, and the Mössbauer method. Chemical analysis was also performed to determine the contents of FeO, Fe_2O_3, and TiO_2. Here we will discuss the results obtained from the chemical analysis and the X-ray diffraction method. The other results will be discussed in the near future.

It is convenient to show the chemical composition of the series B together with the series A as a ternary system: FeO, Fe_2O_3, and TiO_2. Figure 7 shows the chemical composition of the series A and B. It is well known that there exist three solid solution series in the FeO–Fe_2O_3–TiO_2 system at high temperatures: Fe_3O_4–Fe_2TiO_4(titanomagnetite with spinel type), Fe_2O_3–$FeTiO_3$(rhombohedral), and Fe_2TiO_5–$FeTi_2O_5$(orthorhombic). These are shown in Fig. 7 as straight lines. The oxygen reaction lines are also drawn by straight lines. For example, if the stoichiometric composition M in Fig. 7 is oxidized, then the composition moves along the oxygen reaction line to a point N. Some chemical compositions deviate from these oxygen reaction lines. These are due to errors in the chemical analysis. The points on the curved dotted line give the chemical compositions of the series A. The letter x means the mole fraction of Fe_2TiO_4 in the Fe_3O_4–Fe_2TiO_4 solid solution. The values of the Ti/Fe_{total} ratio of 0.071 and 0.304 which were seen in this paper

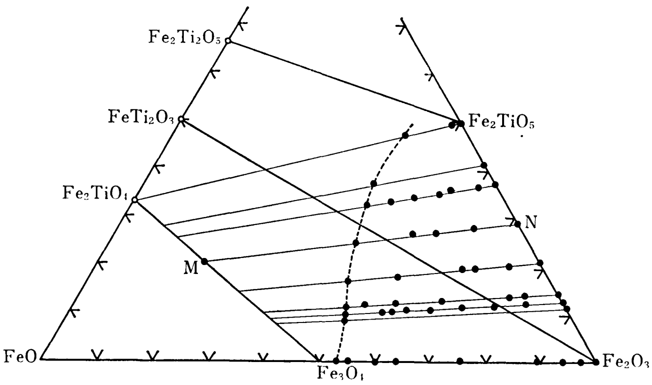

Fig. 7. The chemical composition of the series A and B expressed as FeO, Fe_2O_3, and TiO_2. Three solid solutions of Fe_3O_4-Fe_2TiO_4, Fe_2O_3-$FeTiO_3$ and Fe_2TiO_5-$FeTi_2O_5$ are given by three straight lines. The *oxygen reaction lines* are also shown by the straight lines.

correspond to the mole fractions of 0.2 and 0.7, respectively. As seen in Fig. 7, it is clear that the series A is oxidized, and the chemical composition of the series B is strongly oxidized, depending on the heating temperature and time. When we heated the series A at 200 or 300 °C for 15—20 h, then the products were completely oxidized. At high temperatures, the phase obtained by the complete oxidation of $x=1$ should be pseudobrookite (Fe_2TiO_5), and the compositions in between Fe_2TiO_5 and Fe_2O_3 should be composed of both hematite(Fe_2O_3) and pseudobrookite, if the system is in an equilibrium state.

(5) *The Identification of Phases in the Series A and B.* The X-ray powder diffraction method was adopted to identify the phases present. Infrared spectroscopy was also used to identify the presence of the α-FeOOH phase. Some examples of the diffraction patterns are shown in Fig. 8. Sample series A and B have a spinel type structure irrespective of the oxidation degree and of the Ti/Fe_{total} ratio.

Recently, Readman and O'Reilly[11] and Nishikawa *et al.*[12] have studied the magnetic properties of oxidized (cation-deficient) titanomagnetite (the Fe_3O_4–Fe_2TiO_4 solid solution which naturally occurs). They have synthesized the oxidized titanomagnetite by grinding the stoichiometric solid solution prepared at high temperatures, and have determined the relationships among the chemical composition, the magnetic susceptibility, and lattice constant of the oxidized titanomagnetite. However, it was very hard to obtain any extremely oxidized titanomagnetite with relatively large particles. Thus, the peak intensity of the powder X-ray pattern was very weak, and some people[13] do not believe in the existence of the extremely oxidized titanomagnetite. The particle size of the series A and B ranges from 1000 to 2000 Å,** and the peak intensity is strong enough to determine the precise lattice constant.

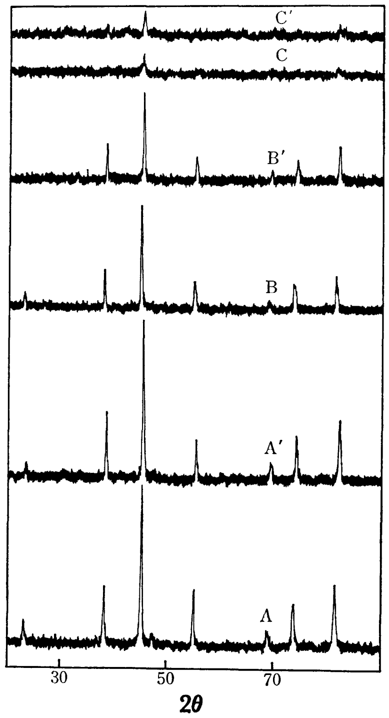

Fig. 8. The X-ray diffraction of the series A and B with radiation of Fe *Kα* (Mn filtration). A: series A with $x=0$. A′: Heated the sample A at 200 °C for 15 h in air, B: series A with $x=0.5$, B′: Heated the sample B at 200 °C for 15 h, C: Series A with $x=1$, C′: Heated the sample C at 300 °C for 15 h.

(6) *The Relationship between the Lattice Constant and the Oxidation Degree of the Spinel Type Solid Solution.* In this paper, we define the oxidation degree(OD) of each oxidized spinel type solid solution as follows:

OD=number of vacant sites/maximum number of vacant sites when completely oxidized.

Table 1 shows the relationship between the mole fraction of Fe_2TiO_4 in the solid solution and the maximum number of the vacant sites when the stoichiometric solid solution was completely oxidized. The lattice constants of completely oxidized samples are also given in Table 1. As seen here, the lattice constant is almost identical in spite of the different mole fractions of Fe_2TiO_4. This fact was suggested qualita-

TABLE 1. THE MAXIMUM NUMBER OF THE VACANT SITES, IN THE SPINEL TYPE STRUCTURE OF THE COMPLETELY OXIDIZED Fe_2TiO_4-Fe_3O_4 SOLID SOLUTION (BASED ON 4 OXYGEN) AND THE LATTICE CONSTANTS MEASURED IN THIS STUDY (Å=0.1 nm)

Mole fraction of Fe_2TiO_4(=a)	Max. number of vacant site(=M)	Lattice constant/Å ±0.001
0	0.333	8.342
0.200	0.391	8.344
0.235	0.401	8.345
0.348	0.433	8.342
0.500	0.474	8.344
0.512	0.477	8.345
0.695	0.524	8.345
0.700	0.526	8.343
0.782	0.547	8.344
1.000	0.600	8.345 (±0.003)

** Å=0.1 nm.

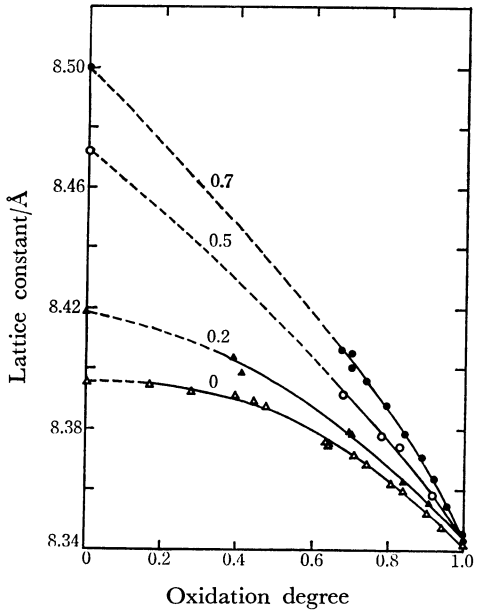

Fig. 9. The relationship between the lattice constant of the series A and B and the oxidation degree. Numbers mean the value *x*.

tively by Readman and O'Reilly.[10] Figure 9 shows the relationship between the oxidation degree of the series B and the lattice constant. As seen here, the lattice constant decreases gradually with increasing the oxidation degree in each sample with the same mole fraction of Fe_2TiO_4. The precise lattice constants of the stoichiometric Fe_2TiO_4–Fe_3O_4 solid solution have been determined by Katsura *et al.*[14] When we extrapolate the present results to the stoichiometric composition (OD=0), all curves fit the points for the stoichiometric solid solution.

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