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Behaviour of Manganese in Oxide of Fe-Mn-O System†

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Abstract

The behaviour of manganese oxide added in wüstite was investigated with the means of electrical conductivity, X-ray profile analysis, and lattice parameter, and Mössbauer resonance measurements. From the electrical conductivity variation as a function of manganese oxide content at constant temperature and oxygen partial pressure, the different conduction behaviours of three regions were observed.

I. Introduction

The role of slag in the ferrous and nonferrous metallurgy and welding is the most important matter because it plays refining behaviour of impure elements such as sulfur, phosphorus and so on from the molten metals. Although the investigations on the physical properties of the slag in the system MO (or M_2O)- SiO_2 have been done by Bockris and co-workers¹⁻⁴⁾, the study concerning structure is still inadequate.

Furthermore, the study of transition metal oxides is necessary because they are always included in the slag during the refining processes.

The Fe-O System

Phase diagram on the system Fe-O was accomplished by Darken and Gurry⁵⁾, and the existence of the wider region of wüstite having defect structure has drawn much attention.

Since Koch and C. Wagner⁶⁾ published a paper concerning defect structure of various transition metal oxides, the relationship between semiconducting property and defect structure has been pursued by many investigators⁷⁻¹¹⁾. As for wüstite, the measurements of lattice parameter of the quenched specimen were performed by Jette and Foote¹²⁾, Benard¹³⁾; and Wills and Rooksby¹⁴⁾, and Levin and J. B. Wagner¹⁵⁾, and the decrement of the lattice parameter with the increment of O/Fe ratio were reported. High temperature X-ray measurements were reported by us¹⁶⁾ and Hayakawa, Cohen and Reed¹⁷⁾.

Later, the relationship between the value of X in $Fe_{1-x}O$ and P_{O_2} was confirmed by Smyth¹⁸⁾ and he found that the vacancy concentration is proportional to the 1/6 power of the oxygen pressure using the results obtained by Darken and Gurry⁵⁾. Himmel,

Mehl and Birchenall¹⁹⁾ and Vallet and Raccach²⁰⁾ have reported the similar conclusions. However, from the studies with thermogravimetric means by Swaroop and J. B. Wagner²¹⁾ and with solid electrolyte by Sockel and Schmarzried²²⁾, it was found that the deviation from the tendency of 1/6 power law in the higher region of oxygen partial pressure occurs.

Likewise, the study of the defect structure was carried on with an electrical conductivity and a thermoelectric measurements. Tannhauser²³⁾ proposed the electron transfer model between octahedral and tetrahedral sites in the wüstite crystal. Anbrey and Marion²⁴⁾ have derived the equation for the electrical conductivity $\sigma = k(V_{Fe}^m)$ at the temperature region of 632~916°C, where k and V_{Fe} are constant and the number of iron vacancy, respectively and electron holes m' produced at the vacancy formation that introduce electrical conduction. Geiger, Levin and J. B. Wagner²⁵⁾ have reported that it occurs the transition from 1/6 power low at 1060°C to 1/3.6 power low at 850°C. In the same way, Bransky and Tannhauser²⁶⁾ have found the transition of p-to-n type at higher oxygen contents.

On the other hand, Roth²⁷⁾ has employed neutron diffraction study for quenched wüstite specimen and he concluded that the movement of cation to the positions of interstitial or tetragonal sites occurs at higher oxygen contents.

Recently, from the studies by thermodynamical, structural and electrical conductivity measurements, the interesting reports which indicated the variation of the defect ordering in the single wüstite phase have appeared.

Vallet and Raccach²⁰⁾ have said that there exist in three regions with different structure of wüstite, and that they are based on the vacant ordering. Fender

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and Riley²⁸⁾, who used electrochemical means, have found that there exist three regions depending on order-disorder transformation in despite of some differences from the result of Vallet and Raccach²⁰⁾.

The Mn-O System

As for the system Mn-O, MnO, Mn₂O₃ and MnO₂ are known to exist as stable phases. Comprehensive study of MnO phase was performed by Davis and Richardson²⁹⁾, who found the O/Mn ratio of MnO depends on oxygen partial pressure and the ratio change from unity to 1.045. Dusquenoy and Marion³⁰⁾ found that MnO may be p-type or n-type depending upon the oxygen partial pressure over the temperature range 900-1200°C and they derived the defect model. Hed and Tannhauser³¹⁾ determined the MnO-Mn₃O₄ phase boundary and showed the relationship between isotherms of the electrical conductivity and $\log[P_{\text{Co}}/P_{\text{Co}}]$ at constant temperature and found that the conductivity of MnO behaves differently in three regions. Eror and J. B. Wagner³²⁾ studied the nonstoichiometric disordering in single crystalline MnO and concluded that the behaviour of MnO is different in only two regions controversial with regard to the existence of three regions described above and both of them fit to $\pm 1/6$ power law.

The Fe-Mn-O System

It is found that a complete solid solution between MnO and FeO can be formed. However, according to our experiment³³⁾ as for non-metallic inclusions manganese killed steel, no clear solution from the formation of their simple solid solution has been given. For this reason, there is a difficulty that FeO as well as MnO is apt to solve in the extraction process. In general, iodine-alcohol solution is used as extracting agent to steel. We used special agent for mild extraction, and various inclusions were determined. It is important to study on the behaviour of the binary oxide in order to know the deoxidation property of manganese in steels.

In this paper, electrical properties of binary oxide having various Fe/Mn ratios were investigated. For comparison with previous studies, thermogravimetric and defect structural studies as for wüstite have been done.

Furthermore, to obtain the information as for defect structure of wüstite and mangano-wüstite, X-ray diffraction profile analysis, high temperature X-ray diffraction and Mössbauer resonance studies were performed.

2. Experimental Procedures

Hematite made from ferrous oxalate and Mn₃O₄

obtained from manganese carbonate as the starting materials were used.

To get mangano-wüstite having various ratio of Fe/Mn, both were thoroughly mixed in acetone and they were heat-treated at 1400°C for 1 hr in Pt crucible. According to Muan and Somiya³⁴⁾, complete solid solution between them is formed at 1400°C in air. Chemical analysis of these materials was performed by emission spectroscopy. Impure elements, which have great effect on the electrical property, were compared with standard Spex Mix. The experimental conditions and the results are given in **Table 1**.

Table 1. Chemical analysis of starting materials (%).

	Si	Ca	Mn	Fe	Mg	Cu	Al	Cr
Mn ₃ O ₄	0.00002	0.0192	—	nil	+	—	—	—
Fe ₂ O ₃	0.083	0.0256	0.256	—	+	++	+	+—

Exp. Conds.

Apparatus, Evert type spectrometer (Shimazu Seisaku Co. Ltd.)

High resolution spectrometer type III (")

Emission stand type 9010 (Spex Co. Ltd.)

Plate, Kodak SA-1 Grating, 1200 lines/mm (2.4 Å/mm)

Secondary voltage, 200 V Secondary current, d—c 5 A

Slit width, 20 μ Analysis interval, 4 mm Sample side, (+)

Electrode, 3 mmφ × 3 mm Exposure, 30 sec Atm., in air

The sintered specimens were recrushed in acetone, and the particle size was controlled. The specimen having 12 mm cube was formed under the pressure of 6 ton/cm² and it was re-heat-treated at 1400°C for 1 hr. For the measurement of porosity, apparent density by JIS M8716 and true density by modified JIS M8716 were determined. Porosity can be calculated with following equation,

$$P = (S_t - S_A) / S_t \times 100$$

where p is porosity (%), S_t is true density and S_A is apparent density. The results obtained are given in **Table 2**.

Table 2. Specific gravity and porosity of the specimens

Fe/Mn	S _t	S _A	P (%)
*10/0	5.48	3.66	33.3
* 9/1	5.60	4.20	25.1
7/3	4.76	3.94	17.2
5/5	4.89	3.86	21.1
4/6	4.77	3.56	25.3
* 2/8	5.34	3.49	34.7
* 0/10	5.24	3.32	36.8

* denotes specimen after experiment.

To exclude contact resistance of the specimen, Pt paste was used, which is made from powdered Pt of 100~250 mesh and non-ionic surface agent and ethyl alcohol solution.

Both surfaces of specimen was washed and slowly heated to 1400°C and holded for 1 hr. And then, Pt paste was rewashed and Pt plate (20 mm ϕ , 0.2 mm thickness) was laid on the specimen and the similar heat-treatment was repeated. Two Pt wire (0.5 mm ϕ) were spot-welded to Pt plate and led to the measuring circuit. Upper electrode was depressed with spring. D-c method was applied and voltmeter (Yokogawa Hewlet Packard Model 4304A) and standard resistor (0.1 Ω , 10 Ω) were used. Electrical current of about 100 mA was passed to electrode. Experimental apparatus is shown in Fig. 1.

Thermogravimetric measurement was done with semi-micro balance (Chōu Keiryōki Co. Ltd.). Various mixed gases, H₂, CO₂ and CO, were supplied by Seitetsu Chemical. They were ultrapure grade. Mixed gases having various ratio of CO₂/CO, 9/1, 4/1, and 1/1 and 1/4, were offered by the maker too. Chemical analyses of gases are given in Table 3. Gases having miscellaneous ratios were produced by gas mixer³⁵⁾.

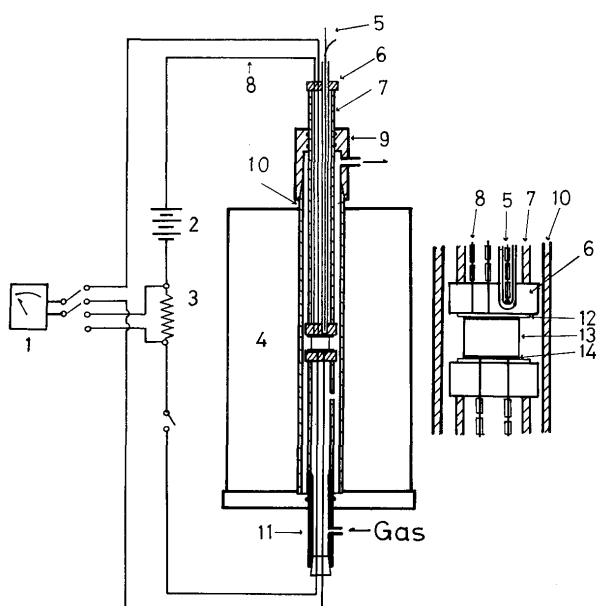


Fig. 1. Apparatus for Conductivity Measurement.

1. Voltmeter 2. Battery 3. Standard Resistance 4. Pt-Furnace
5. Thermocouple 6. Al₂O₃-Plate 7. 10 Al₂O₃-Tube 8. Pt-Wire
9. Brass Jacket 11. Brass Tube 12. Pt-Plate 13. Specimen
14. Pt-Paste

Table 3. Chemical analysis of gases used. (ppm)

	H ₂ O	O ₂	CH ₄	H ₂
CO ₂	—	2	20	—
H ₂	tr.	2-3	—	99.9 %

To confirm profile analysis of X-ray diffraction, wüstite and mangano-wüstite specimens were quenched into ice-cooled mecury after kept at 1350°C in the solid state and at 1500°C in the liquid state for 1 to 5 hrs. CoK α radiation filtered with iron was used. To take off the X-ray instrumental errors, silicon powder as the standard specimen was used. Each line profiles of (111), (200) and (200) were obtained with the fixed count method. To obtain accurate profiles of higher order diffraction of mangano-wüstite, the most intense X-ray diffraction was used. Fourier analysis by Stokes³⁶⁾ was carried out with computer and the integrated intensity was calibrated with the values already given^{9), 36-38)}.

High temperature X-ray diffraction was performed with photographic method by Rigaku high temperature camera (type 1211/M2).

The electrical conduction measurement of wüstite melt under the various oxygen partial pressures were carried out at 1500°C with d-c four terminal method. Pt-20 %Rh crucible was used. Cell constant was obtained with IN potassium chloride aqueous solution. Electrical conductivity κ was calculated from the following equation

$$\kappa = (I/V) \cdot (l/s)$$

, where κ is the electrical conductivity (mho/cm), I is the intensity (A), and V is the voltage (V) and l/s is the cell constant (cm⁻¹) respectively. Experimental apparatus is shown in Fig. 2.

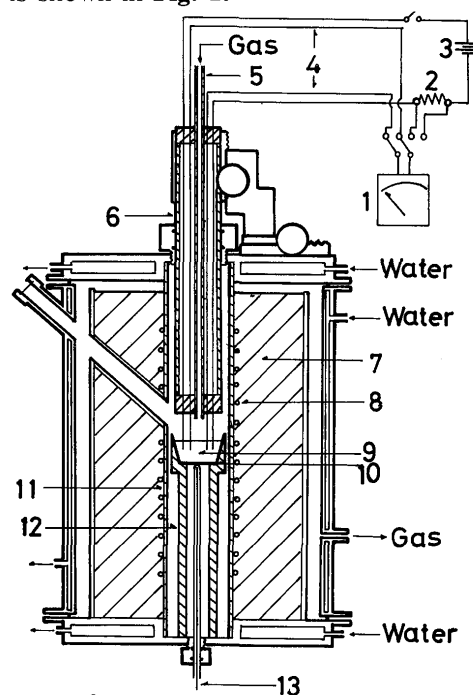


Fig. 2. Apparatus for measurement.

1. Volt meter 2. Standard reesistance 3. Battery 4. Pt-wire
- 5, 6, 11, 12. Al₂O₃-tube 7. Bubbled Al₂O₃ 8. Pt-furnace 9. Melt
10. Pt-crucible 13. Thermocouple

The Mössbauer spectrometer is composed of the electromagnetic velocity and the γ -ray counting systems. The Mössbauer resonance analyzer (Elron #5011) of the linear velocity type connected to a multi-channel analyzer. The source of γ -ray is ^{57}Co (5 and 30 m Ci) diffused into stainless steel and palladium and are attached to the velocity transducer to provide Doppler shift. The line width observed with the source against thin iron foil absorbers was 0.35 mm/sec.

A proportional counter filled with a mixed gas of 95 %Xe and 5 %N₂ was used for the detection of 14.4 KeV γ -ray. The velocity scale was calibrated with pure iron as a standard absorber. Specimens used for this experiment are given in **Table 4**.

Table 4. Composition of specimens and the isomer shift values (δ)

Specimen	Temp (°C)	Holding Time (Hr)	Mn (%)	CO ₂ /CO	δ
W -1	1350	1	0	1/1	1.000
WM-1	1350	1	1	4/1	1.0104
WM-2	1350	1	3	4/1	0.9792
WM-3	1500	1	0.5	4/1	0.9792
WM-5	1500	3	3	4/1	0.9354

Theory⁷⁾

FeO and MnO are oxygen-excess compounds over the most of their range of existence. From the difference of the ionic radii between metallic cation and oxygen, metal vacancies may be introduced through the reaction of oxygen with the oxide



Correspondingly, the metal vacancy with one or two effective negative charges and one or both of the holes are formed depending on the temperature

$$V_M^x = V_M' + h^\cdot, \text{ etc.} \quad (2)$$

The defect equilibria describing the formation of single neutral metal vacancies and the subsequent excitation of electron holes in MO may be expressed for small defect concentration

$$[V_M^x] = K_1 P_{\text{O}_2}^{1/2} \quad (3)$$

$$[V_M'] p = K_e [V_M^x] \quad (4)$$

$$[V_M''] p = K_r [V_M'] \quad (5)$$

where $p = [h^\cdot]$ denotes the concentration of electron holes.

From the electroneutrality conditions, it leads

$$P = [V_M^x] + 2[V_M''] \quad (6)$$

Through combinations of Eq. 3—6 the concentration of the separate point defects and p can be evaluated.

$$P^3 = K_1 K_e P_{\text{O}_2}^{1/2} (2K_r + p) \quad (7)$$

As for oxygen vacancies, two limiting conditions must be considered. (1) At low values of p ($p \ll 2K_r$), then

$$P = (2K_1 K_e K_r)^{1/3} P_{\text{O}_2}^{1/6} \quad (8)$$

while at (2) high values of p ($p \gg 2K_r$), then

$$p = (K_1 K_e)^{1/2} P_{\text{O}_2}^{1/4} \quad (9)$$

The total concentration of the metal vacancies correspondingly changes from $P_{\text{O}_2}^{1/6}$ through $P_{\text{O}_2}^{1/2}$.

CO₂-CO Equilibrium³⁹⁾

From the equilibrium reaction,



the equilibrium constant K is obtained as follows:

$$K = P_{\text{O}_2} \cdot P_{\text{CO}}^2 / P_{\text{CO}_2}^2$$

At constant temperature,

$$P_{\text{O}_2} = 1/K \cdot (P_{\text{CO}}/P_{\text{CO}_2})^2$$

so the following relation is obtained

$$\log P_{\text{O}_2} \propto 2 \log P_{\text{CO}} / P_{\text{CO}_2}$$

3. Experimental Results and Discussions

Thermogravimetric Study of Wüstite

The nonstoichiometry as a function of temperature and oxygen partial pressure has been studied by several investigators^{7)~11)}. All the papers have recognized that linear relationship between them exists. **Fig. 3** shows the variation of O/Fe ratio as a function of P_{O_2} at various temperatures. Linear changes of O/Fe ratio were verified in agreement with the previous findings. However, the value of P_{O_2} equilibrating with FeO having the decided defect structure is somewhat different from the value by Darken and Gurry⁵⁾. Using H₂/CO₂ mixed gas, thermal segregation in the

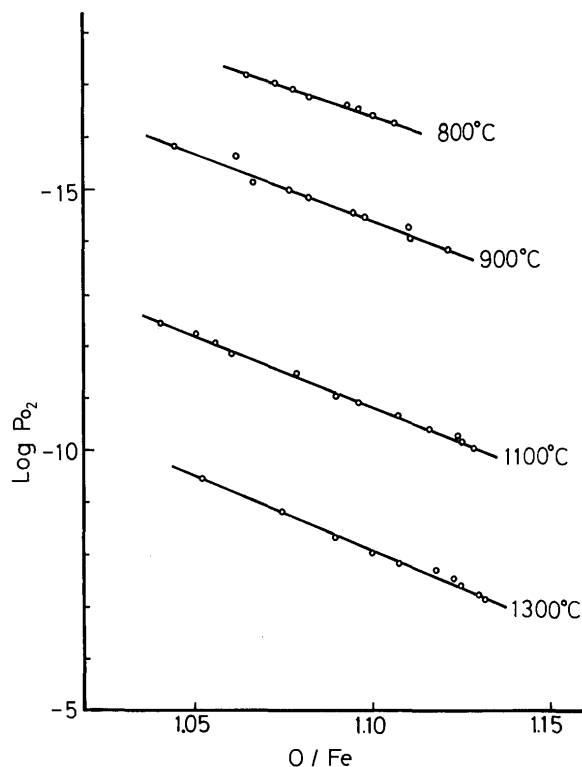


Fig. 3. Variation of O/Fe as a function of P_{O_2} at various temperatures.

gases probably occurs. On the thermogravimetric study, CO_2/CO mixed gas does not use, because it necessitates refractory tube having large caliber and to avoid leak of toxic gases.

Figure 4 shows cation deficiency as a function of

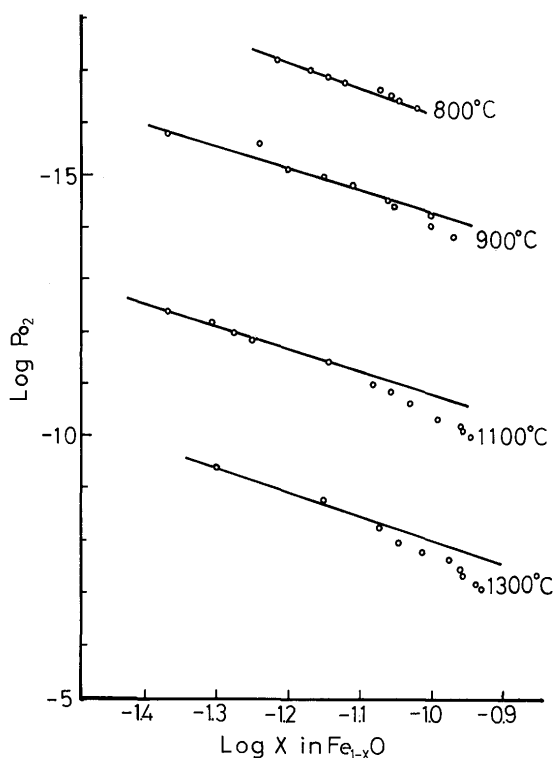
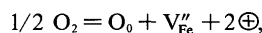


Fig. 4. Cation deficiency, $\text{Log } X$, in Fe_{1-x}O as a function of $\text{Log } P_{O_2}$.

the oxygen partial pressure as for FeO. The vacancy concentration is proportional to the $1/6$ power of the oxygen partial pressure and hence the reaction establishing the nonstoichiometry is



where the symbol, V_{Fe}'' , denotes a cation vacancy with no associated electron holes, and the symbol, \oplus , denotes an electron hole. Sockel and Schmarzried²² have reported that the slope of $1/6$ power begins to deviate and reaches to the slope of $1/8$ power where wüstite-magnetite transition occurs. Likewise, Swallop and J. B. Wagner²¹ have supported this finding. In our results, the same behaviour of the slope was found. For this deviation from $1/6$ to $1/8$ power, the following reason should be considered. It is emphasized that the equilibrium constant relates the activities of the structure elements involved in the defect reaction, but under ideal conditions and when the structure elements can be assumed to be randomly distributed over available sites, the activities are equal to the concentrations of the structure elements. This is a valid assumption in dilute solutions. However, when ordering of defects occurs or when the defects are not randomly distributed due to mutual interactions of the defects, etc., the activities have to be used instead of concentrations. Raccach and Vallet²⁰, Carel and Vallet⁴¹ and Carel, Wiegel and Vallet⁴² have reported that there are three different regions within FeO domain labeled I, II and III. The existence of three different regions may be associated with order-disorder transitions, but the viewpoint of structure as for transition is an open question. As an example, the time for the equilibrating in the thermogravimetric studies is shown in Fig. 5. It is anticipated that the longer time is necessary to carry out the reducing experiment from magnetite to wüstite.

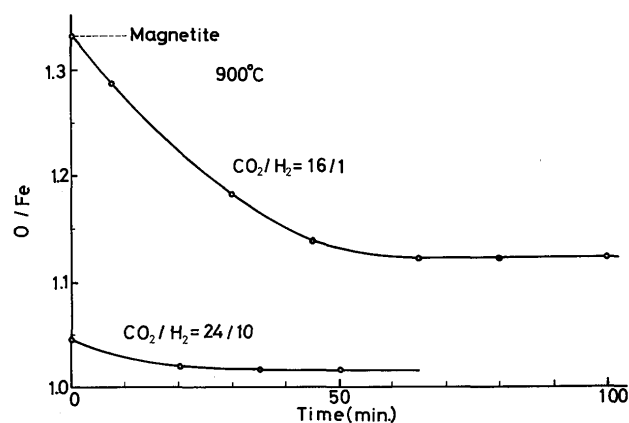


Fig. 5. Variation of O/Fe with time.

Electrical Conductivity

Figure 6 and 7 show electrical conductivity results of manganowüstite having various ratio of Fe/Mn as

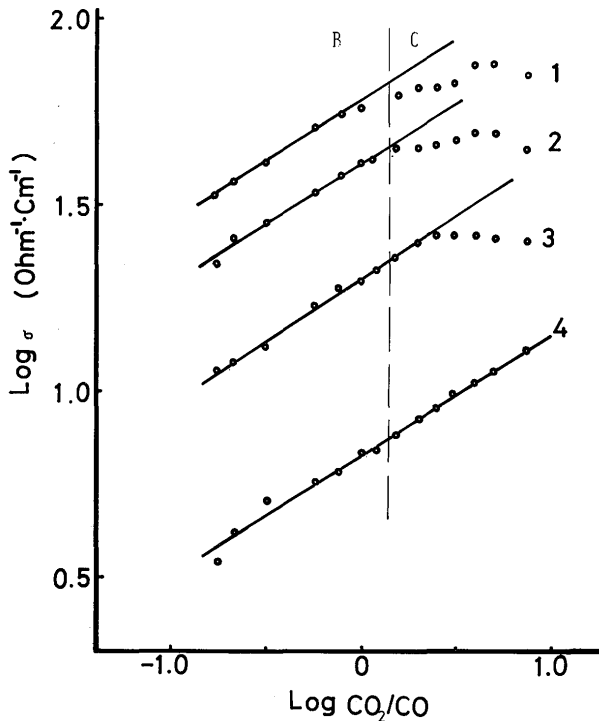


Fig. 6. Electrical conductivity on various composition of manganowüstite at 1300°C.
Fe/Mn ratios (1) 10/0, (2) 9/1, (3) 8/2, (4) 6/4.

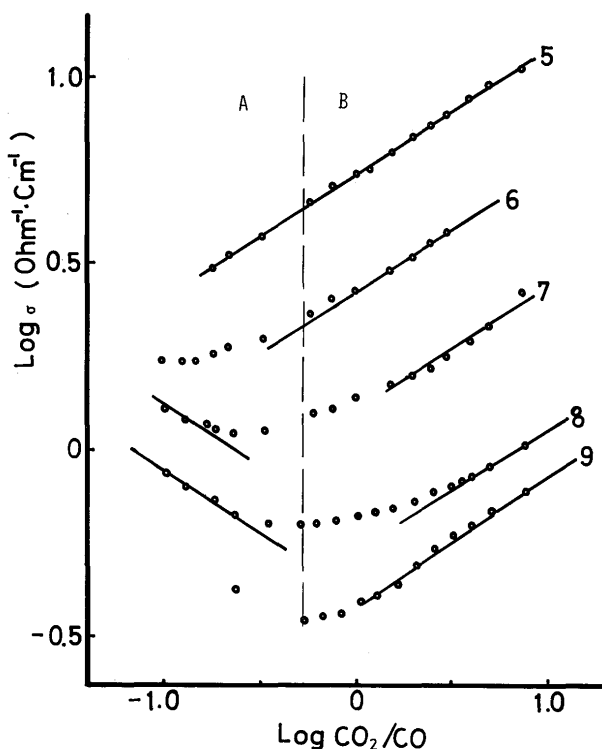


Fig. 7. Electrical conductivity on various composition of manganowüstite at 1300°C.
Fe/Mn ratios (5) 5/5, (6) 7/3, (7) 2/8, (8) 1/9, (9) 0/10.

a function of the partial pressure of oxygen (ratio of P_{CO_2}/P_{CO}) at 1300°C. Curve 1 shows the change of $\log \sigma$ between 1.5~1.8. Geiger, Levin and J. B. Wagner²⁵⁾ have reported the change of $\log \sigma$ between 1.93—2.25 at 1000°C. It is appropriate value because of $\log \sigma$ wüstite becomes greater with the rise of temperature. However, the difference of the specimens used should be considered. They corrected thickness of sample by using initial thickness and lattice constant of wüstite, and the influence of porosity may be important in our case. In the region of low oxygen partial pressure, it is seen that $\log \sigma$ is proportional to 1/6 power of P_o , but it is apparent from curve 1 that plots of $\log \sigma$ tend to exhibit curvature at the higher oxygen concentrations as well as the results obtained by the thermogravimetric study.

The curve approaches to the maximum value and shows transition. This is the representation of p-to-n transition of wüstite. The interpretation of this transition mechanism are not tenable. However, the defect structural models presented must be examined. Neutron diffraction study by Roth²⁷⁾ indicated that the defects in wüstite could be considered as "microdomains" of magnetite in wüstite. From the further studies of superstructure peaks from wüstite, the presence of long-range order have been suggested^{43), 44)}. With the increase of manganese content in manganowüstite, the linear relation of 1/6 power law are notable as shown at the curves 4 and 5. With further increase of manganese content, p-to-n transition appears at the lower oxygen partial pressure. This finding is in agreement with the previous results.

Until now, Dusquenoy and Marion³⁰⁾, Hed and Tannhauser³¹⁾, and Eror and J. B. Wagner³²⁾, and O'Keeffe and Valigi⁴⁵⁾, and Bocquett, Kawahara and Lacombe⁴⁶⁾ have studied the electrical conductivity of MnO as a function of temperature and oxygen partial pressure. They verified p-to-n transition with the minimum value of $\log \sigma$ at $CO_2/CO=1/1$. The regions which show different behaviours of electrical conductivity have been termed A, B and C (These are described in Fig. 6 and 7). At partial pressures lower than that of the minima (region A) the conductance increases with decreasing pressures, and the oxide is n-conductor, while at higher partial pressures the oxide is p-conductor and the conductivity increases with increasing oxygen pressure. On the other hand, the oxygen partial pressure dependence of the conductivity in which n-type conduction occurs gives $CO_2/CO=1/7.5$, and the value is consistent with the value by Hed and Tannhauser³¹⁾ as for MnO at 1200°C. The clear interpretation of this dependence is not given as well as the abnormal behaviour at higher oxygen partial pressure region.

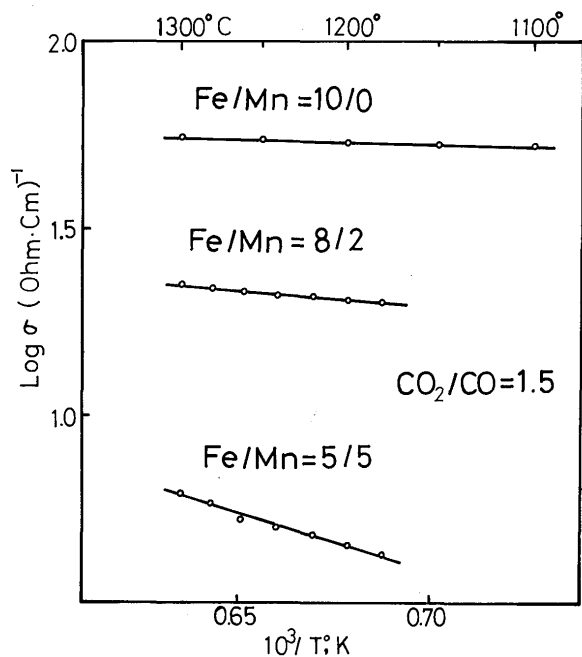


Fig. 8. Variation of electrical conductivity as a function of temperature.

Figure 8 shows electrical conductivity of manganowüstite having various ratio of Fe/Mn as a function of temperature at constant oxygen partial pressure. From this, it is verified that the conduction behaviour are different between the content of Fe/Mn=10/0, 8/2 and 5/5.

Figure 9 shows the electrical conductivity variation as a function of manganese oxide added at constant temperature and oxygen partial pressure. Likewise, the different conduction behaviours of three groups are anticipated.

To explain the different electrical conduction behaviours, structural experiment has been necessitated.

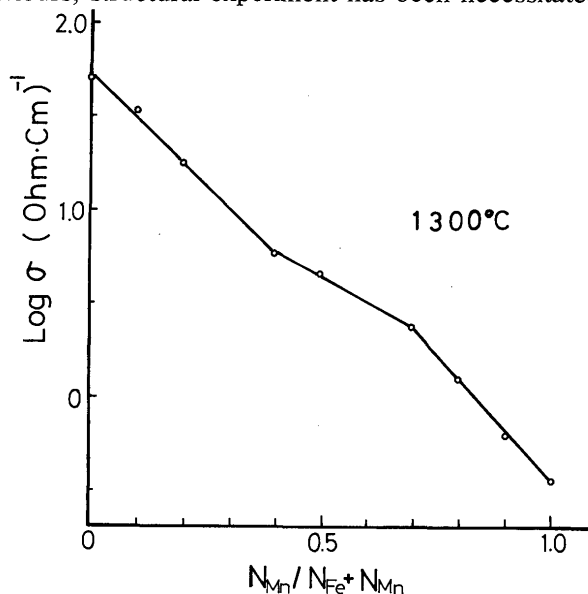


Fig. 9. Variation of conductivity as a function of Mn concentration at $\text{CO}_2/\text{CO}=0.5$.

X-ray Profile Analysis

The defect structure of wüstite has been studied by measuring the integral X-ray intensity of powders quenched from solidus and liquidus regions. The co-existing phase in the specimens used is shown in Table 5. It is apparent that the longer holding time than 3 Hrs. is necessary to bring these specimens to equilibrium. One would expect the effect of instrumental error on the X-ray diffraction profiles from the comparison of $h(x)$ measured with $f(x)$ treated with Fourier analysis in Tables 6 and 7. As an example, line profiles of $f(x)$ of specimens are given in Fig. 10. Structure factor calculated as wüstite takes spinellike structure is given in Table 8. The distribution of Fe^{3+} between octahedral and tetrahedral sites denoted by parameter y introduced by Roth²⁷⁾ and Smuts³⁷⁾ was taken into the calculation. For comparison, structure factor

Table 5. Sample compositions and co-existing phase

Specimen	Temp (°C)	Holding Time (Hr)	Mn (%)	CO_2/CO	Phase
W -5	1350	1	0	4/1	Magnetite
W -9	1500	5	0	4/1	—
WM-1	1350	1	1	4/1	Magnetite
WM-2	1350	1	3	4/1	Magnetite
WM-3	1500	1	0.5	4/1	Magnetite
WM-4	1500	3	3	1/4	Tr. Magnetite
WM-5	1500	3	3	4/1	—

Table 6. Breadth of $h(x)$.

Specimen	(111)	(200)	(220)
W -5	0.27°	0.29°	0.43°
W -9	0.24	0.31	0.32
WM-1	0.24	0.28	0.36
WM-5	0.21	0.23	0.37

Table 7. Breadth of $f(x)$.

Specimen	(111)	(200)	(220)
W -5	0.16°	0.14°	0.25°
W -9	0.16	0.18	0.16
WM-1	0.16	0.17	0.21
WM-5	0.13	0.16	0.20

Table 8. Structure factor ratio.

Specimen	$ F_{200} ^2/ F_{111} ^2$	$ F_{220} ^2/ F_{111} ^2$
$\text{Fe}_{1.0}\text{O}$	2.93	1.87
$\text{Fe}_{0.9}\text{O}$	1.87	2.06

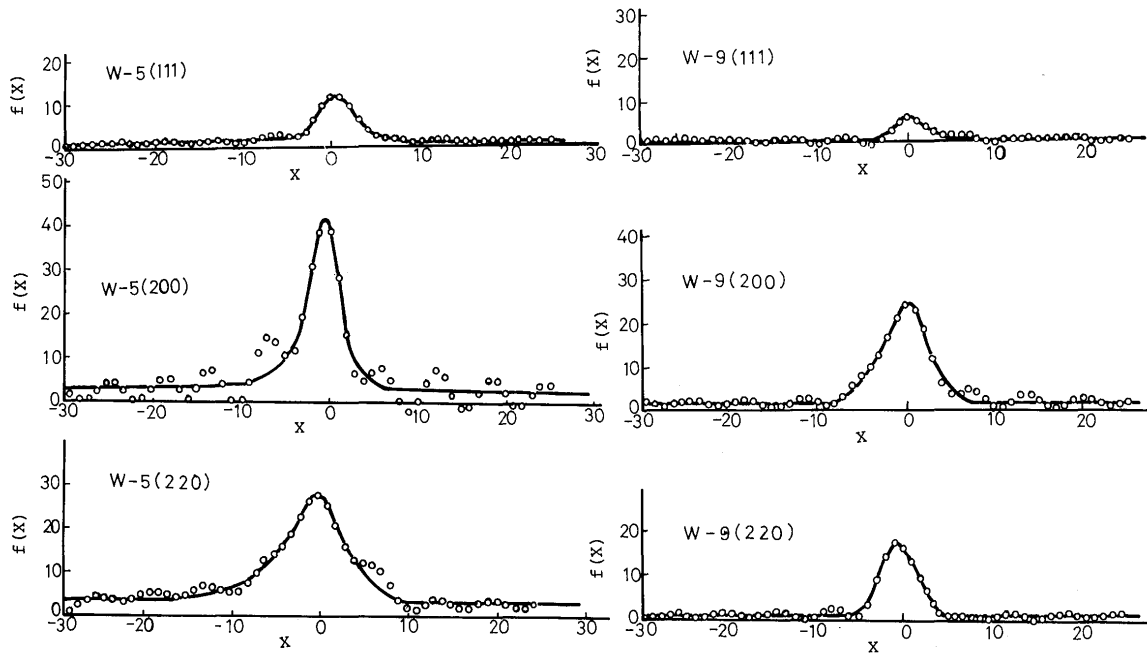


Fig. 10 (a). Profile obtained from fourier analysis.

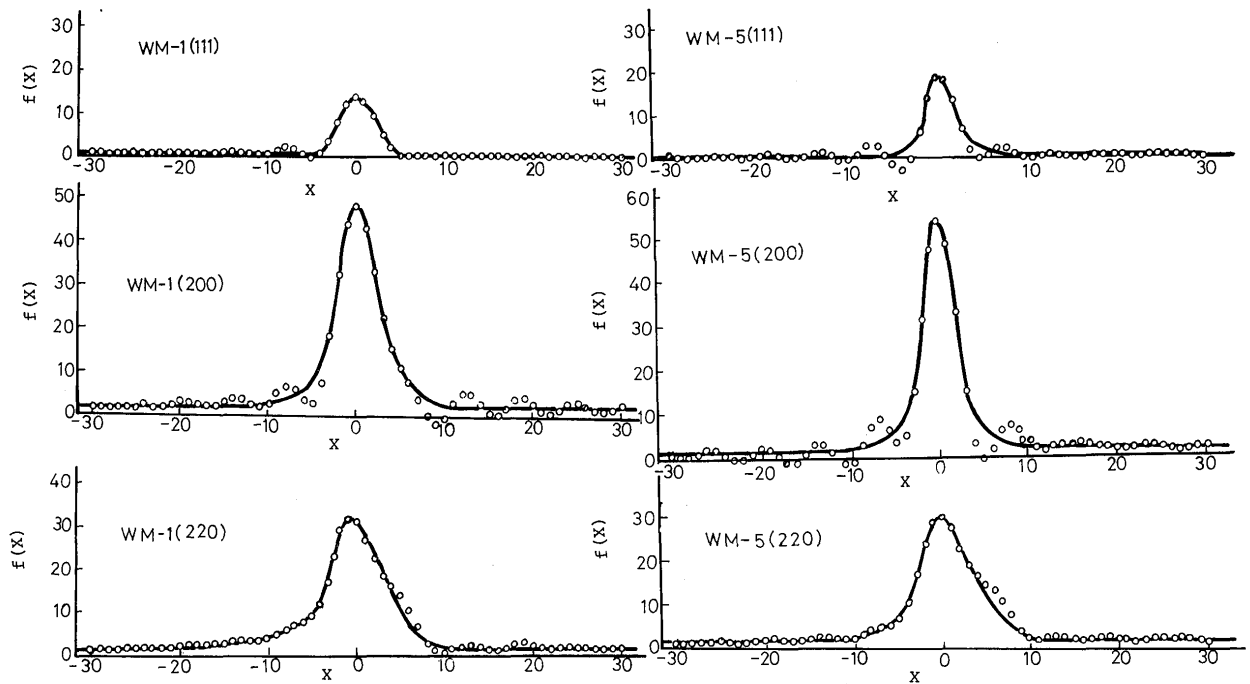


Fig. 10 (b). Profile obtained from fourier analysis.

calculated as taking sodium chloride structure (Fe_{10}O) is given too. In **Table 9**, the structure factor of each

Table 9. Structure factor ratio

Specimen	$ F_{200} ^2/ F_{111} ^2$	$ F_{220} ^2/ F_{111} ^2$
W -5	6.77	7.92
W -9	10.03	6.75
WM-1	7.38	8.03
WM-5	7.11	5.56

specimens are represented. The inconsistency is remarkable to decide what model is apposite to wüstite, so it should be considered if any abnormal situation of X-ray reflection occurs on (111) plane. From the mean dimension of the crystallite of each planes calculated from Scherrer's equation⁴⁷⁾ in **Table 10**, but it was impossible to interpret the cause of the differences. Although another reflections of the higher planes were desired, they were insufficient on account of their weak reflections. Notable difference was not

Table 10. Mean dimension of crystallites (Å).

Specimen	D ₁₁₁	D ₂₀₀	D ₂₂₀
W —5	735	868	562
W —9	735	648	818
WM—1	744	684	644
WM—5	888	764	867

appreciated to specimens quenched from the molten state and the influence of manganese addition was not noticed too. In order to get X-ray profiles of the higher order reflection of mangano-wüstite, more intense X-ray diffraction were used. Profile analysis results of this experiment will be published in near future.

Lattice Parameter Study

The lattice parameters obtained from the quenched specimens are given in Table 11. The important fact of the lattice parameter in mangano-wüstite melt is independent of the manganese content and oxygen partial equilibrated.

Table 11. Lattice parameter of specimens (Å).

Specimen	a ₀	Specimen	a ₀
W —5	4.278 ₀	W —9	4.277 ₄
WM—1	4.285 ₈	WM—3	4.285 ₂
WM—2	4.290 ₇	WM—4	4.285 ₂
		WM—5	4.285 ₂

High Temperature X-ray Diffraction Study

Results of high temperature X-ray diffraction are given in Table 12. We could not agree that magnetite and wüstite are continuous phases³⁷⁾ from the facts, their simultaneous appearance at 800°C when CO₂/CO ratio is 4/1, different expansion behaviours and electrical conductivity change. Interplanar spacings of wüstite and magnetite under various experimental conditions are given in Table 13.

Table 12. Results of high temperature X-ray diffraction.

CO ₂ /CO	Temp.(°C)	Phases
9/1	1300	M
	1200	M
	1100	M
	1000	M
4/1	1250	W
	1100	W
	1000	W
	900	W
	800	W+M
	600	M
1/1	500	M
	1000	W
	900	W
1/4	800	W
	1100	γ—Fe

W: wüstite, M: magnetite

Table 13 (a) Interplanar spacings of magnetite (Å).

(hkl)	Standard value	Sp. quenched	High temp. diff.	
		CO ₂ /CO=9/1 1300°C	CO ₂ /CO=9/1 1000°C	CO ₂ /CO=9/1 1200°C
220	2.963 ₈	2.982 ₇	3.016 ₀	3.011 ₆
311	2.530 ₅	2.533 ₈	2.570 ₉	2.591 ₁
400	2.097 ₀	2.104 ₆	2.122 ₃	2.130 ₆
422	1.711 ₉	1.717 ₃	1.729 ₆	1.734 ₈
511	1.613 ₁	1.618 ₄	1.634 ₈	1.636 ₆
440	1.482 ₇	1.491 ₃	1.498 ₁	1.499 ₆

Table 13 (b). Interplanar spacings of wüstite (Å).

(hkl)	Sp. quenched	High temp. diff.		
	CO ₂ /CO=4/1 1300°C	CO ₂ /CO=1/1 1000°C	CO ₂ /CO=4/1	
			900°C	1100°C
111	2.486 ₂	2.525 ₂	2.518 ₄	2.518 ₈
200	2.148 ₆	2.186 ₉	2.173 ₇	2.175 ₉
220	1.517 ₂	1.541 ₂	1.536 ₃	1.540 ₈
a ₀	4.287 ₀	4.347 ₅	4.347 ₅	4.350 ₇

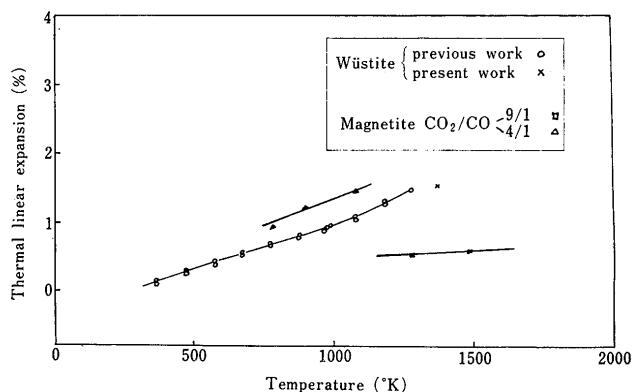


Fig. 11. Thermal linear expansion values of wüstite and magnetite.

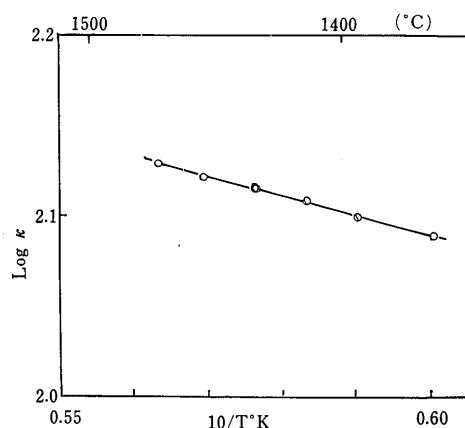


Fig. 12. Variation of electrical conductivity of wüstite melt as a function of temperature.

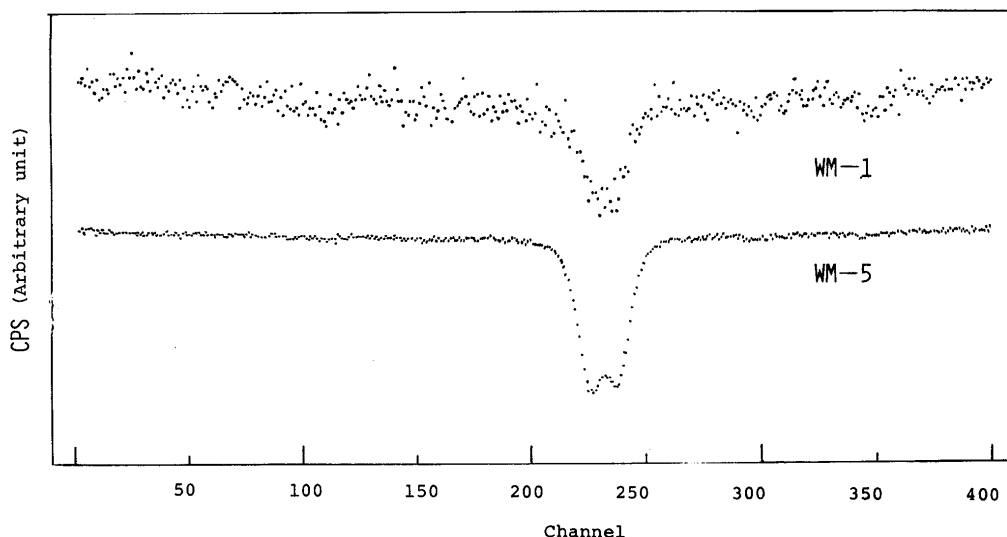


Fig. 13. Mössbauer spectra of mangano-wüstite.

The thermal linear expansion coefficient calculated from high temperature X-ray diffraction analysis was compared with the value obtained from usual expansion experiment⁴⁸⁾. Good agreement as for wüstite was determined, but some irregularities were certified in magnetite. These tendencies are shown in **Fig. 11**.

Electrical Conductivity of Wüstite Melt

The dependency of the electrical conductivity on the oxygen partial pressure of wüstite melt was not determined.

It must be considered that the corrosion of Pt-20 %Rh crucible used occurs, so the choice of sample holder is necessitated. Result obtained is shown in **Fig. 12**. Semi-conduction characteristic and the value of conductivity have shown good agreement with the value previously given⁴⁹⁾.

Mössbauer Resonance Study

Mössbauer spectra of mangano-wüstite are shown in **Fig. 13**. In **Table 14**, isomer shift values are given. Profile analysis to separate two quadrupole splits Fe^{2+} and a Fe^{3+} singlet is now proceeding. In near future, the information as for defect structure will be published.

4. Summary

The behaviour of manganese oxide added in wüstite was studied with various physical methods. From the electrical conductivity measurement, it was anticipated that there are three regions which show different conduction tendency with the manganese oxide content in wüstite. With the results obtained

from X-ray diffraction profile analysis, Mössbauer resonance analysis and so on, the abnormal behavior of manganese will be clarified in future.

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