



TITLE:

# On the Constitution of Zinc-ferrite

AUTHOR(S):

KUSHIMA, Isao; AMANUMA, Tsuyoshi

---

CITATION:

KUSHIMA, Isao ...[et al]. On the Constitution of Zinc-ferrite. Memoirs of the Faculty of Engineering, Kyoto University 1954, 16(4): 191-204

ISSUE DATE:

1954-12-25

URL:

<http://hdl.handle.net/2433/280309>

RIGHT:

# On the Constitution of Zinc-ferrite

By

Isao KUSHIMA and Tsuyoshi AMANUMA

Department of Metallurgy

(Received July, 1954)

## 1. Introduction

Zinc-ferrite is known as the compound of the equimolar of ZnO and  $\text{Fe}_2\text{O}_3$  as  $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$  or  $\text{ZnFe}_2\text{O}_4$ , and distinguished from other various ferrites, such as  $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ ,  $\text{NiO}\cdot\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ , as its structure is a normal spinel type as  $\text{CdO}\cdot\text{Fe}_2\text{O}_3$ , and is non-magnetic.

For the physical and electrical properties of various ferrites, many important results are obtained, but the chemical constitution of ferrites is not generally known up to the present except in a few instances. In a previous paper<sup>1)</sup>, the authors reported on formation temperature and the formation ratio of zinc-ferrite. At that time, it seemed that zinc-ferrite ( $\text{ZnFe}_2\text{O}_4$ ) was capable of forming a solid solution with  $\text{Fe}_2\text{O}_3$  or ZnO and forming ferrite of various molar ratio ( $\text{ZnO}:\text{Fe}_2\text{O}_3$ ) depending upon the condition of formation. Pertaining to this point, the authors have conducted a research on the constitution of the compounds between ZnO- $\text{Fe}_2\text{O}_3$  system and also inquired into the formation of magnetite in this system.

## 2. Preparation of Samples

ZnO was prepared from purified  $\text{ZnSO}_4$  and its purity was over 99.0%.  $\text{Fe}_2\text{O}_3$  was prepared from ferrous oxalate. It is said that ferrous oxalate is decomposed and oxidized between 180°C. to 280°C. in the air<sup>2)</sup>. In our case, ferrous oxalate was heated at 600°-650°C. in the air for more than 5 hours.

$\text{Fe}_2\text{O}_3$  and ZnO were mixed so that the molar ratio of  $\text{ZnO}:\text{Fe}_2\text{O}_3$  became exactly 1:4 (Sample No. 2), 1:3 (No. 32), 1:2 (No. 33), 2:3 (No. 3 or 34), 4:5 (No. 35), 1:1 (No. 4 or 36), 5:4 (No. 37), 3:2 (No. 5 or 38), 7:3 (No. 8), 3:1 (No. 10), 4:1 (No. 6), and 9:1 (No. 9). These mixed samples were pressed in the mould into tablets of 15 mm. diameter and about 3 mm. wide or into square bars of 5 mm.<sup>2</sup> × 50 mm. under 50-75 kg./cm.<sup>2</sup> pressure and they were sintered at 800°, 1000°,

1150°, 1250°, 1350°, and 1440°C. for many hours. Table 1 shows the analyses of these samples.

Table 1. Analyses of the various Samples.

Sample No.	Chemical analysis		Molar ratio of ZnO:Fe <sub>2</sub> O <sub>3</sub>	Results of X-ray study
	ZnO (Wt. %)	Fe <sub>2</sub> O <sub>3</sub> (Wt. %)		
1 or 31	—	100	—	Observed only Fe <sub>2</sub> O <sub>3</sub> lattice
2	11.7	88.3	1 : 4	Observed Fe <sub>2</sub> O <sub>3</sub> and ZnFe <sub>2</sub> O <sub>4</sub>
32	13.0	87.0	1 : 3.4	"
33	20.8	79.2	1 : 2	Observed only ZnFe <sub>2</sub> O <sub>4</sub>
3 or 34	25.2	74.8	2 : 3	"
35	28.8	71.2	4 : 5	"
4 or 36	33.9	66.1	1 : 1	"
37	39.0	61.0	5 : 4	Observed ZnFe <sub>2</sub> O <sub>4</sub> and ZnO
5 or 38	43.2	56.8	3 : 2	"
8	55.2	44.8	7 : 3	"
10	59.4	40.6	3 : 1	"
39	64.2	35.8	3.5 : 1	"
6	68.3	31.7	4 : 1	"
9	81.0	19.0	8.5 : 1	"
7	100	—	—	Observed only ZnO

### 3. Experimental Method

Each sintered tablet sample was crushed under 100 mesh and photographed by the Debye-Scherrer X-ray. The magnetic property was measured with the sintered square bar sample. After these experiments, the sample was chemically analysed and i) free ZnO, ii) constitution of the ferrite (ZnO:Fe<sub>2</sub>O<sub>3</sub>), iii) and the concentration of magnetite were determined. The free ZnO in the sample was leached in

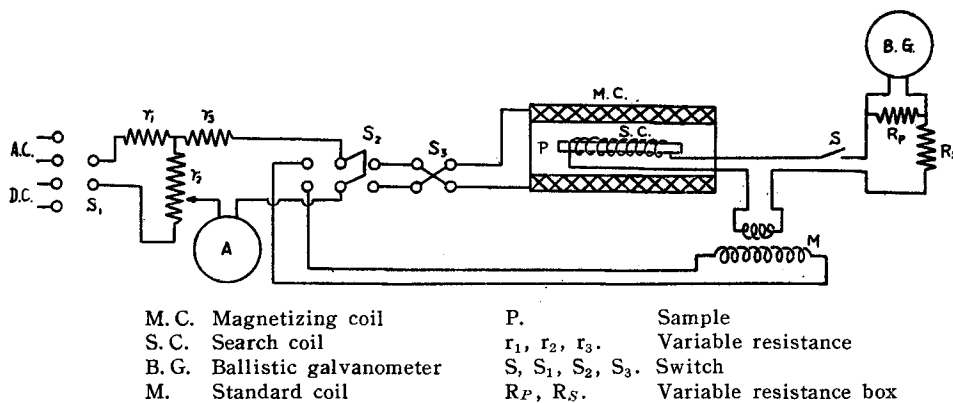


Fig. 1. Measurement apparatus of the magnetic property of samples.

ammoniac ammonium chloride solution. The magnetite concentration was determined from  $\text{Fe}^{++}$  percent which was decided by dissolving the sample in 1:1 HCl solution under  $\text{CO}_2$  atmosphere, and immediately titrated by the 0.1N.  $\text{KMnO}_4$  solution.

The intensity of magnetization and H-I curves of samples were both obtained by the ballistic galvanometer method shown in Fig. 1.

#### 4. Experimental Results

##### A. Electrical resistance

The resistivity of the sample was measured by Wheatstone bridge at room temperature. Plotting the value of  $\log \rho$  attained as a function of constitution of zinc-ferrite, Fig. 2 is obtained. Table 2 shows the value of  $\rho$  measured. The 1-1 ferrite (No. 4 or No. 36) shows the least resistivity, and when the ferrite forms a solid solution with  $\text{Fe}_2\text{O}_3$ , the value rises slightly. On the contrary, existence of the free ZnO makes the  $\rho$  remarkably high.

In Fig. 2, it seems that the samples 1-4, 2-3, and 1-1 (No. 2, 3 and 4) belong to one group, and the samples 3-2, 7-3, 3-1, 9-1 and ZnO (No. 5, 8, 10, 9 and 7) belong to another group.

##### B. X-ray experiments

The X-ray diffraction patterns of the samples are shown in photo. 1~20 together with the X-ray diffraction picture of magnetite. All of these pictures were taken by the same Debye-Scherrer camera with iron radiation. Since the X-ray diffraction photograph of zinc-ferrite are very much alike that of magnetite and when they exist together, they cannot be distinguished from each other. The chemical constitution of the sample investigated by X-ray is shown in Table 1.

Photo. 1 shown the X-ray diffraction pattern of the mixed sample of ZnO and  $\text{Fe}_2\text{O}_3$ . This photograph contains the patterns of ZnO and  $\text{Fe}_2\text{O}_3$ .

Photo. 2 shows the X-ray figure of pure  $\text{Fe}_2\text{O}_3$  heated at  $1250^\circ\text{C}$ . for 3 hours. Only the pure  $\text{Fe}_2\text{O}_3$  pattern is seen and the pattern of  $\text{Fe}_3\text{O}_4$  could not be observed.

Photo. 3 shows the X-ray figure of the 1-3 sample (No. 32) sintered at  $1250^\circ\text{C}$ . for 3 hours. Here, the patterns of zinc-ferrite and free  $\text{Fe}_2\text{O}_3$  both could be seen.

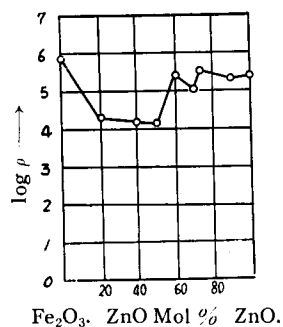


Fig. 2.  $\rho$  value of various samples.

Table 2. Value of  $\rho$

Sample No.	Resistivity ( $\Omega$ cm.)
1	$7.15 \times 10^5$
2	$1.9 \times 10^4$
3	$1.4 \times 10^4$
4	$1.3 \times 10^4$
5	$2.3 \times 10^5$
8	$9.7 \times 10^4$
10	$2.9 \times 10^5$
9	$1.7 \times 10^5$
7	$1.8 \times 10^5$

Photo. 4, 5 and 6 show the X-ray figures of the 1-2, 2-3, and 1-1 samples (No. 33, 3 or 34, and 4 or 36) respectively sintered at 1250°C. for 3 hours. They all show only the complete spinel (zinc-ferrite) pattern and that of free  $\text{Fe}_2\text{O}_3$  could not be observed even in the ferrite containing initially as high as 81.5 wt. pct. (66.6 mol pct.)  $\text{Fe}_2\text{O}_3$ , could not be observed.

Photo. 7, 8, 9, 10 and 11 respectively show the X-ray figures of the 3-2, 7-3, 3-1, 4-1, and 9-1 samples (No. 5 or 38, 8, 10 or 39, 6, and 9) heated at 1250°C. for 3 hours. They all show the patterns of zinc-ferrite and free ZnO. The more the quantity of ZnO, the more distinct the pattern of ZnO.

Photo. 12 shows the X-ray figure of the pure ZnO.

Photo. 13 shows the X-ray figure of 2-3 sample (No. 34) heated at 1150°C. for 3 hours, and it contains the patterns of both zinc-ferrite and free  $\text{Fe}_2\text{O}_3$ . But the pattern of free  $\text{Fe}_2\text{O}_3$  in photo. 13 is weaker compared with that in photo. 14, which shows the X-ray figure of the 2-3 sample (No. 34) heated at 1000°C for 3 hours.

Photo. 15 shows the X-ray figure of 2-3 sample (No. 34) annealed at 800°C. for 2 hours after being heated at 1250°C. for 3 hours. This picture is very much similar to photo. 14, and it is obvious that the  $\text{Fe}_2\text{O}_3$  is educed from the solid solution of zinc-ferrite and  $\text{Fe}_2\text{O}_3$  by annealing.

Photo. 16, 17, 18, and 19 show the X-ray figures of 3-2 sample (No. 5 or 38) heated for 3 hours at 800°, 1000°, 1200°, and 1250°C. respectively, and the decreasing strength of the pattern of free ZnO with the increase of the heating temperature can be seen.

Photo. 20 shows the X-ray figure of natural magnetite, which is very much alike that of zinc-ferrite (Photo. 6).

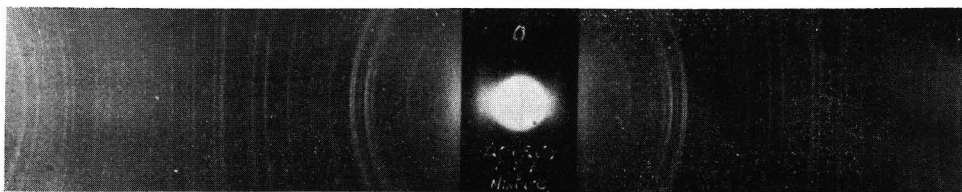


Photo. 1. Mixed Sample of ZnO and  $\text{Fe}_2\text{O}_3$ .

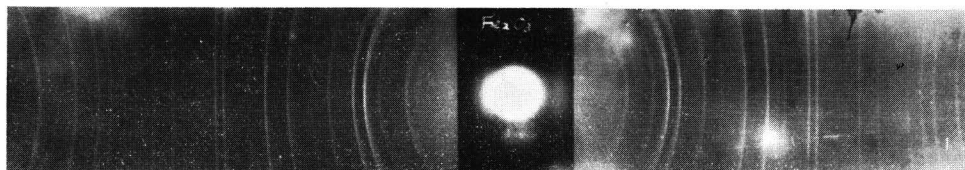


Photo. 2.  $\text{Fe}_2\text{O}_3$  (No. 1) heated at 1250°C.

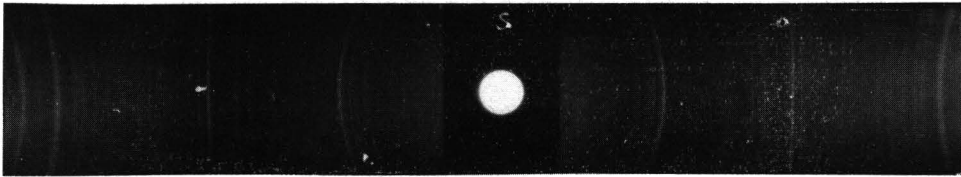


Photo. 3. 1-3 Sample (No. 32) heated at 1250°C.

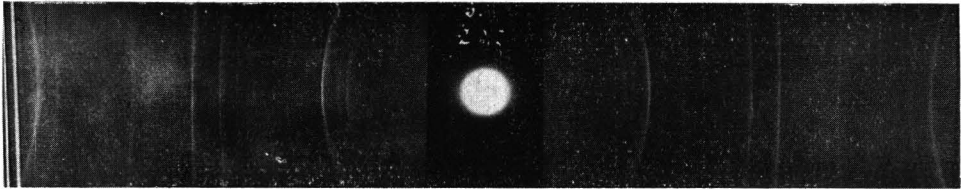


Photo. 4. 1-2 Sample (No. 33) heated at 1250°C.

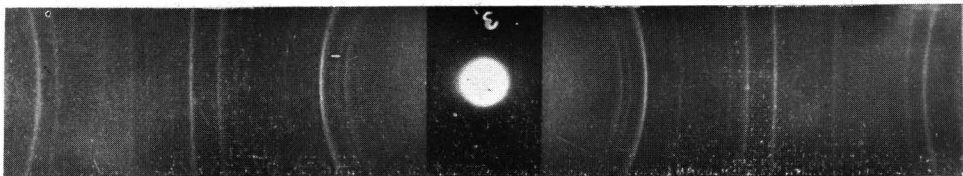


Photo. 5. 2-3 Sample (No. 3 or 34) heated at 1250°C.

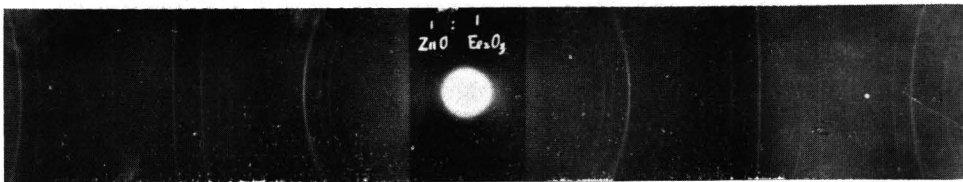


Photo. 6. 1-1 Sample (No. 4 or 36) heated at 1250°C.

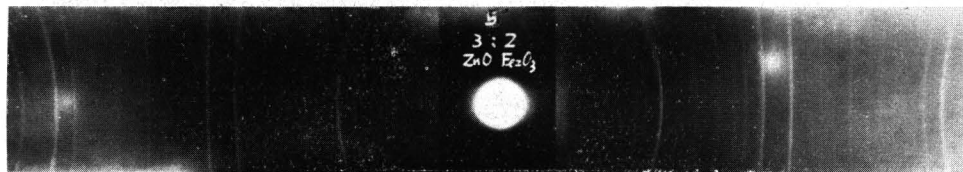


Photo. 7. 3-2 Sample (No. 5 or 38) heated at 1250°C.

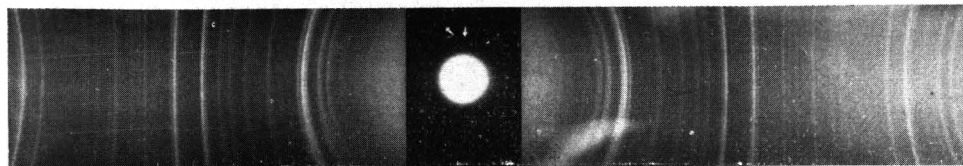


Photo. 8. 7-3 Sample (No. 8) heated at 1250°C.

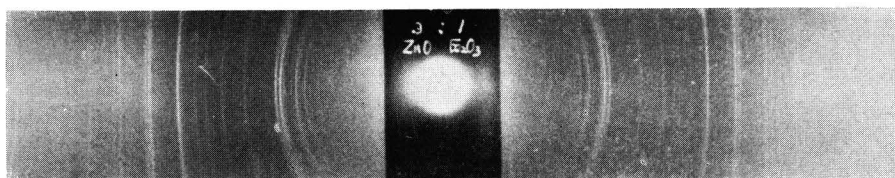


Photo. 9. 3-1 Sample (No. 10 or 39) heated at 1250°C.

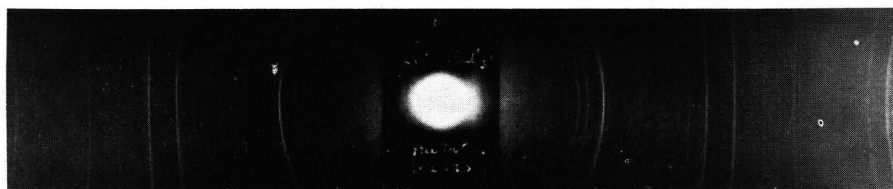


Photo. 10. 4-1 Sample (No. 6) heated at 1250°C.

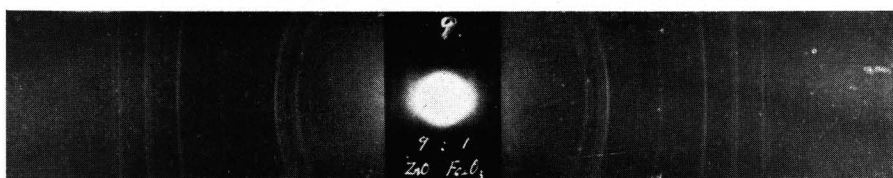


Photo. 11. 9-1 Sample (No. 9) heated at 1250°C.

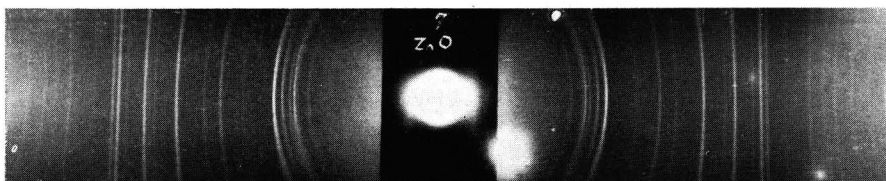


Photo. 12. ZnO (No. 7) heated at 1250°C.

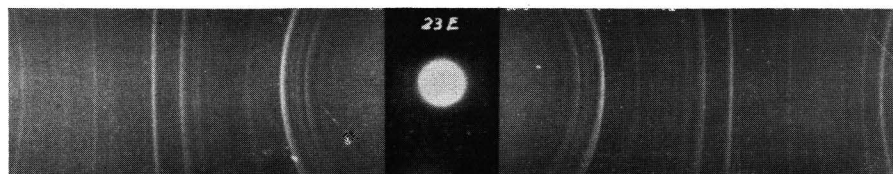


Photo. 13. 2-3 Sample (No. 3 or 34) heated at 1150°C.

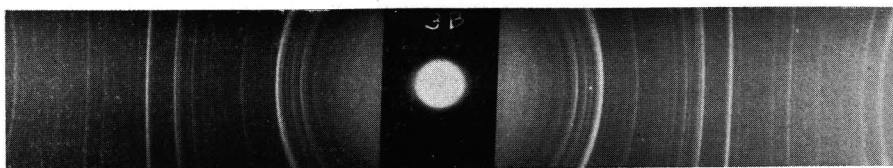


Photo. 14. 2-3 Sample (No. 3 or 34) heated at 1000°C.

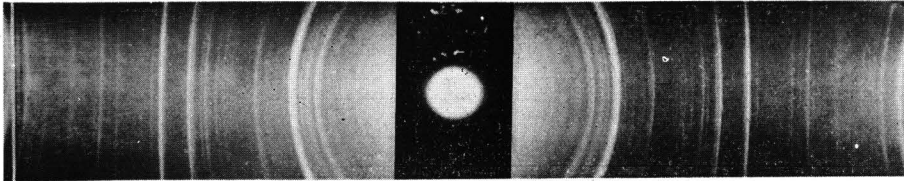


Photo. 15. 2-3 Sample (No. 3 or 34) annealed at 800°C.

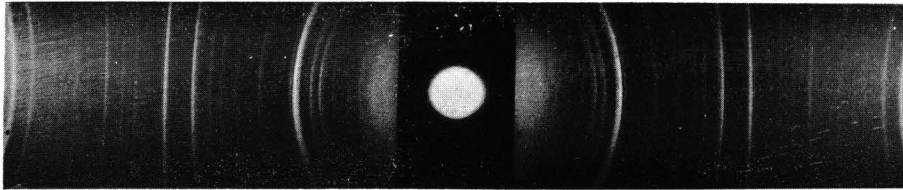


Photo. 16. 3-2 Sample (No. 5 or 38) heated at 800°C.

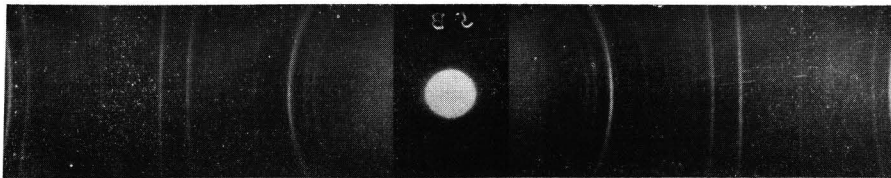


Photo. 17. 3-2 Sample (No. 5 or 38) heated at 1000°C.

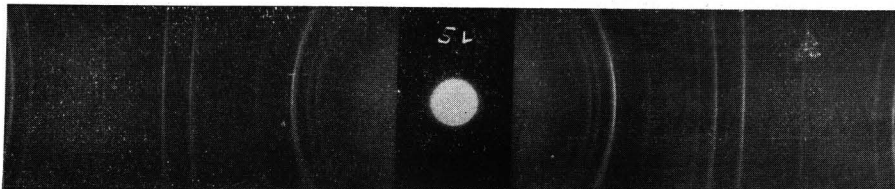


Photo. 18. 3-2 Sample (No. 5 or 38) heated at 1200°C.

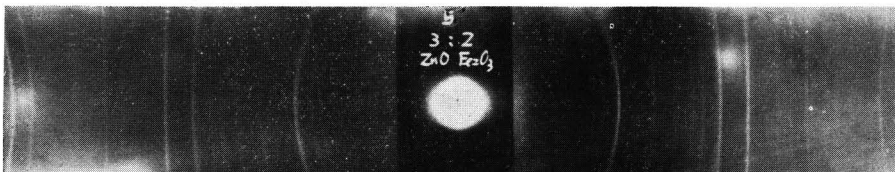


Photo. 19. 3-2 Sample (No. or 38) heated at 1250°C.

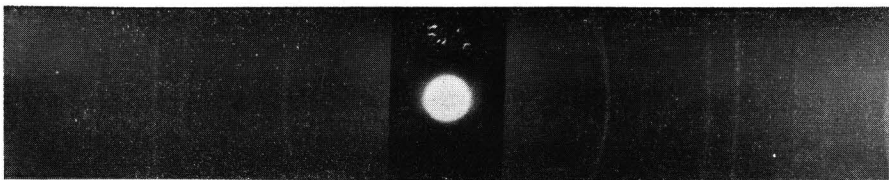


Photo. 20. Natural Magnetite.



The calculated values of  $d$  of  $\text{Fe}_2\text{O}_3$ , zinc-ferrite and  $\text{ZnO}$  are shown in Table 3.

Table 3.  $d$  Values of Samples

No.	No. 1 $\text{Fe}_2\text{O}_3$		$\text{Fe}_2\text{O}_3$		No. 4 $\text{ZnFe}_2\text{O}_4$		$\text{ZnFe}_2\text{O}_4$		No. 7 $\text{ZnO}$		$\text{ZnO}$	
	$d$ .	I.	$d$ .	I.	$d$ .	I.	$d$ .	I.	$d$ .	I.	$d$ .	I.
1	4.075	v.w.			3.23	v.w.			3.06	w.		
2	3.611	w.	3.68		2.933	s.	2.97	s.	2.808	w.		
3	3.05	s.			2.77	w.			2.771	s.	2.81	s.
4	2.687	v.s.	2.69	v.s.	2.51	v.s.	2.53	v.s.	2.705	w.		
5	2.435	v.s.			2.075	v.w.			2.568	s.		
6	2.187	s.			1.744	v.w.			2.44	v.s.	2.46	v.s.
7	1.915	v.w.			1.70	v.w.	1.71		2.07	v.w.		
8	1.827	s.	1.84	s.	1.612	v.w.			1.89	s.	1.91	
9	1.688	v.s.	1.69		1.60	s.	1.61		1.774	w.		
10	1.627	v.w.			1.474	s.	1.484	s.	1.612	v.s.	1.61	s.
11	1.59	w.	1.60		1.30	v.w.			1.536	v.w.		
12	1.48	v.s.	1.485	s.	1.24	v.w.	1.24		1.480	v.w.		
13	1.446	v.s.	1.452	s.	1.121	w.	1.122		1.464	v.s.	1.474	s.
14	1.307	s.	1.308		1.096	s.	1.093		1.396	v.w.		
15	1.252	w.	1.259		1.048	w.	1.049		1.371	v.s.	1.378	s.
16	1.185	w.			0.991	v.w.			1.35	s.	1.355	
17	1.165	w.	1.163						1.29	v.w.	1.302	
18	1.137	w.							1.229	w.	1.236	
19	1.109	s.	1.104						1.197	v.w.		
20	1.053	v.s.	1.056						1.173	v.w.	1.179	
21	1.035	v.w.							1.143	v.w.		
22	0.986	w.							1.088	v.s.		
23									1.072	v.w.		
24									1.058	w.	1.063	
25									1.039	v.s.	1.042	
26									1.011	v.s.	1.016	

v.s. very strong s. strong w. weak v.w. very weak

Of special interest to note from the results of these X-ray experiments, are the followings. i), The 1-1 sample (No. 4 or 36) furnishes the complete spinel structure by heating at  $800^\circ\text{C}$  for 3 hours. ii), When the sample contain excess  $\text{Fe}_2\text{O}_3$  over 1:1 ratio, the excess  $\text{Fe}_2\text{O}_3$  gradually dissolves in the zinc-ferrite ( $\text{ZnFe}_2\text{O}_4$ ) and by the heat of up to  $1250^\circ\text{C}$ . a solid solution whose ratio of  $\text{ZnO}:\text{Fe}_2\text{O}_3$  is up to 1:2 is formed. In other words, the solubility limit of  $\text{Fe}_2\text{O}_3$  in the solid zinc-ferrite ( $\text{ZnFe}_2\text{O}_4$ ) is about 33 mol. pct.  $\text{Fe}_2\text{O}_3$  at  $1250^\circ\text{C}$ . iii), The solid solution of zinc-ferrite ( $\text{ZnFe}_2\text{O}_4$ ) and  $\text{Fe}_2\text{O}_3$  thus obtained, educe the excess  $\text{Fe}_2\text{O}_3$  again when it is annealed at low temperature ( $800^\circ\text{C}$ .). iv), From these results, we obtained the

equilibrium diagram for the system ZnO-Fe<sub>2</sub>O<sub>3</sub> as shown in Fig. 3.

C. Magnetic experiments.

Zinc-ferrite is known as a non-magnetic material belonging to the normal spinel type. But it has been explained by Kato and Takei<sup>4)</sup> that when zinc-ferrite makes a solid solution with magnetite or ferro-magnetic Fe<sub>2</sub>O<sub>3</sub> at high temperature, it assumes ferro-magnetism.

We also conducted our study on magnetic properties of our various zinc-ferrite. In Fig. 4 the H-I curves of magnetite and various kinds of zinc-ferrites are shown. From Fig. 4, it is made clear that the magnetic intensity increased in order of the sample 1-3

(No. 32), 4-5 (No. 35), 2-3 (No. 34) and 1-2 (No. 33). The 1-2 sample (No. 33) has the strongest intensity of magnetization; however, pure Fe<sub>2</sub>O<sub>3</sub> (No. 1) and 1-1 ferrite (No. 4 and 36) do not assume ferro-magnetism even if they are heated at 1250°C. for 3 hours. Since the dissociation of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> originates vigorously when the sample is heated in vacuum, the sample forms a solid solution with magnetite and it shows a stronger intensity of magnetization compared with the

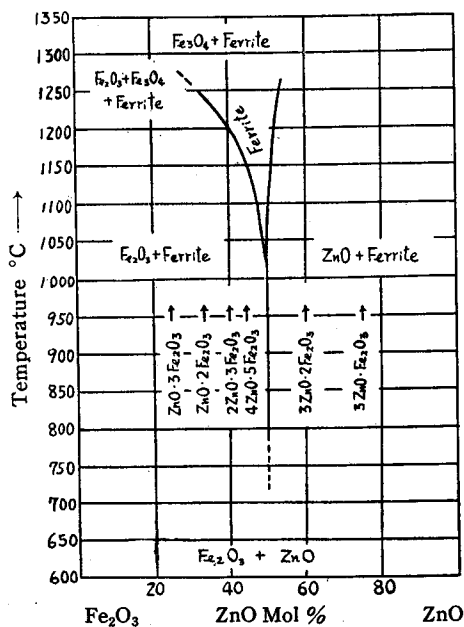


Fig. 3. Phase diagram for the system ZnO-Fe<sub>2</sub>O<sub>3</sub> (in mol. pct.)

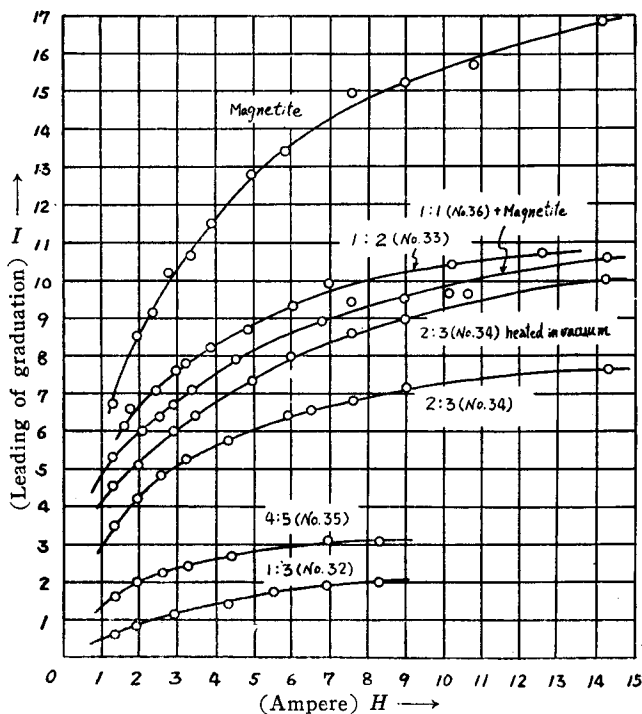


Fig. 4. H-I Curves for various samples.

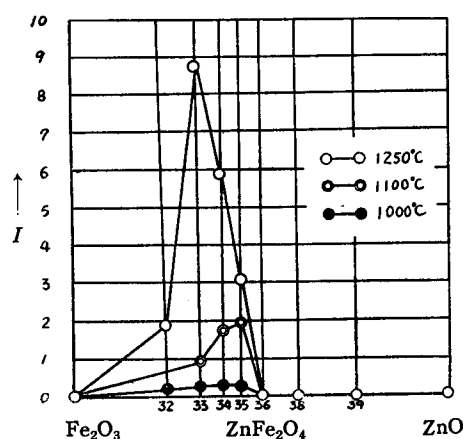


Fig. 5. Intensity of magnetization of various samples.

original ferrite which is heated in the air. This point will be discussed in the latter part of this treatise. Fig. 5 shows the intensity of magnetization of samples of various components under the same magnetic field. The heat treatment has a great effect on the intensity of magnetization of ferrites of the same components. For example, in the 2-3 sample (No. 34), the intensity of magnetization varies decidedly by its heat treatments such as quenching, slow cooling or annealing. As is shown in Table 4, in the case of cooling in the air, the intensity of magnetiza-

tion of the sample is the strongest, which is followed by the case of quenching, and when the sample is cooled slowly or annealed in the furnace, it becomes very weak or non-magnetic. It seems that, in the case of quenching, the sample becomes of more porous structure as compared with the case of air cooling.

Table 4. Intensity of Magnetization of the 2-3 Sample (No. 34) for various heat treatment.

Heating Temp.	Heating Time	Heat Treatment	Intensity of Magnetization
1000°C.	3 hours	air cool	0.2
1100°C.	"	"	1.7
1250°C.	"	"	5.9
"	"	quench	4.3
"	"	slow cool	0.1
"	"	annealed at 800°C. for 2 hours	0.0

The samples with higher ZnO contents does not possess ferro-magnetism by heating them at 1250°C.

From the results obtained, it is surmised that the zinc-ferrite becomes ferro-magnetic when it forms a solid solution with the  $\text{Fe}_2\text{O}_3$ , and presumably this dissolved  $\text{Fe}_2\text{O}_3$  is not ferro-magnetic but is non-magnetic. And the fact that the samples having high  $\text{Fe}_2\text{O}_3$  contents becomes non-magnetic in the case of slow cooling or annealing is due to the eduction of  $\text{Fe}_2\text{O}_3$  from the solid solution. Of course, when the zinc ferrites having high  $\text{Fe}_2\text{O}_3$  contents are heated at a high temperature, a part of  $\text{Fe}_2\text{O}_3$  contained in the sample becomes magnetite and this  $\text{Fe}_3\text{O}_4$  is retransformed into non-magnetic  $\text{Fe}_2\text{O}_3$  in the process of air cooling, and it is

almost non-magnetic  $\text{Fe}_2\text{O}_3$ , not  $\text{Fe}_3\text{O}_4$ , that is dissolved in the solid solution.

D. The formation of magnetite.

From the X-ray studies and chemical analyses, it became clear that the pure  $\text{Fe}_2\text{O}_3$  is dissociated only few quantities by heating it at  $1250^\circ\text{C}$ . But the degree of dissociation of  $\text{Fe}_2\text{O}_3$  by heating varies not only with the temperature, duration of heating and the atmosphere, but also with the presence of other oxides. This is what often occurs in ferrospinels containing excess  $\text{Fe}_2\text{O}_3$  over the stoichiometric (equimolar) amount. On this point, we studied the ratio of formation of magnetite in various kinds of zinc-ferrite. In case of quenching from high temperature, the magnetite formed by dissociation of  $\text{Fe}_2\text{O}_3$  cannot be re-oxidized to  $\text{Fe}_2\text{O}_3$  and the  $\text{Fe}_3\text{O}_4$  content

Table 5. Formation ratio of Magnetite (%)

Sample No.	31	32	33	34	35	36	38	39
ZnO : $\text{Fe}_2\text{O}_3$	—	1 : 3	1 : 2	2 : 3	4 : 5	1 : 1	3 : 2	3.5 : 1
Heating temp.								
1100°C.	0	—	0	0	2	—	—	—
1250°C.	1.5	—	—	14	4.5	2	0.3	0
1350°C.	6.6	24.2	21.6	18.2	—	4.4	4.4	0.9
1440°C.	9.1	26	—	21.6	—	6.3	3.0	—

becomes higher than that in the case of air cooling. The dissociation becomes more vigorous when the samples are heated in vacuum.

Chemical analyses of the air cooling samples containing various ratio of ZnO and  $\text{Fe}_2\text{O}_3$  show that it is not all the excess  $\text{Fe}_2\text{O}_3$  that is dissociated at  $1250^\circ\text{C}$ .,  $1350^\circ\text{C}$ ., or even at  $1440^\circ\text{C}$ ., and the sample presumably becomes a solid solution of  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and a part of  $\text{Fe}_3\text{O}_4$ . In samples containing excess ZnO, only a small portion of  $\text{Fe}_2\text{O}_3$  is dissociated to  $\text{Fe}_3\text{O}_4$  by heating it over  $1350^\circ\text{C}$ . The results of these are shown in Table 5.

F. Phase diagrams for the systems

ZnO- $\text{Fe}_2\text{O}_3$  and ZnO-FeO- $\text{Fe}_2\text{O}_3$ .

By summarizing the above results,

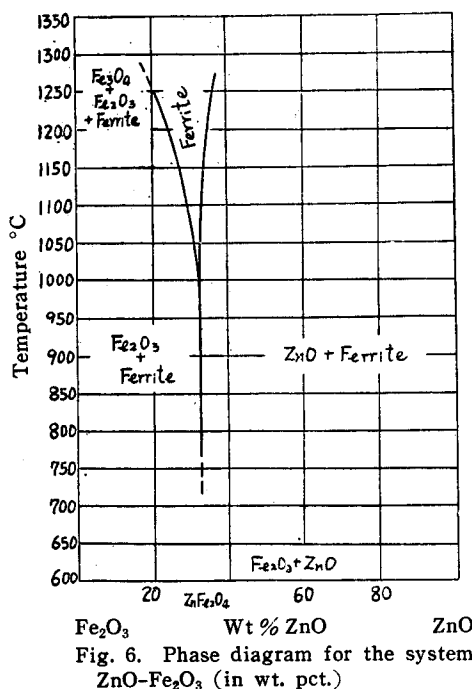


Fig. 6. Phase diagram for the system ZnO- $\text{Fe}_2\text{O}_3$  (in wt. pct.)

the phase diagrams for the systems  $\text{ZnO-Fe}_2\text{O}_3$  and  $\text{ZnO-FeO-Fe}_2\text{O}_3$  are obtained as shown in Fig. 6 and 7.

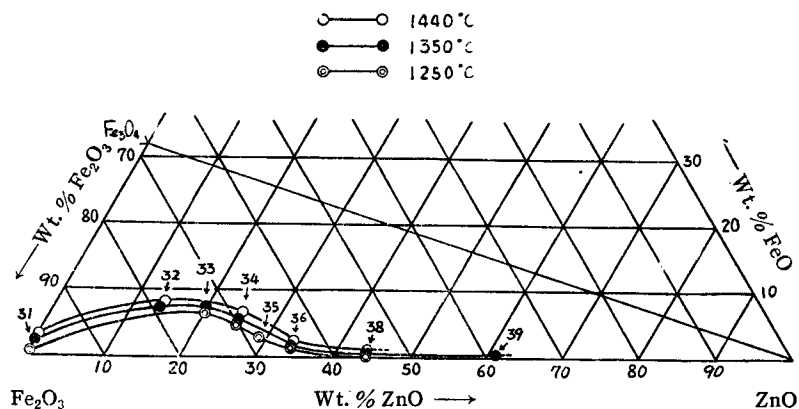


Fig. 7. Phase Diagram for the System  $\text{ZnO-Fe}_2\text{O}_3\text{-FeO}$  (in wt. pct.)

#### 4. Consideration

In zinc-ferrite containing excess  $\text{Fe}_2\text{O}_3$  over the equimolar amount, a part of the excess  $\text{Fe}_2\text{O}_3$  is apt to be dissociated to  $\text{Fe}_3\text{O}_4$ . These  $\text{Fe}_3\text{O}_4$  presumably dissolve in zinc-ferrite, and can be considered that the ferro-magnetism of the zinc-ferrite having a high  $\text{Fe}_2\text{O}_3$  contents is due to formation of the solid solution of zinc-

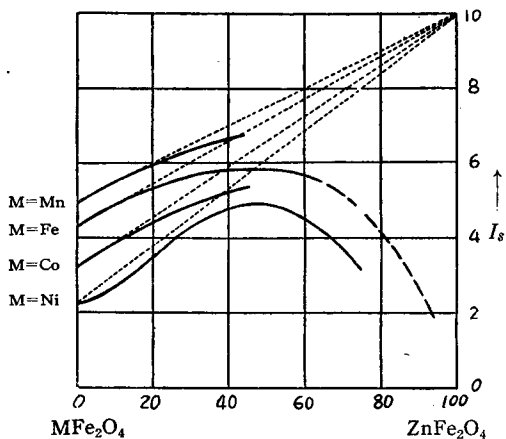


Fig. 8.  $I_s$  curves of various solid solution of ferrites.

ferrite and magnetite. Fig. 8 shows the changes of the intensities of the magnetism when the solid solutions are formed by various proportions of zinc-ferrite and various kinds of ferrite such as Mn-, Fe-, Co-, and Ni-ferrite. From the theory of "Ferri-magnetism" it is expected that the intensity of the magnetization of these solid solutions in each case increases along the dotted lines. According to a literature<sup>9)</sup>, the magnetism intensifies at first as Zn  $\text{Fe}_2\text{O}_4$  is increased and attains the maximum value near the equimolar compound (solid solution). Although it lacks the value on the side of  $\text{ZnFe}_2\text{O}_4$ , it is considered that the  $I_s$  curve concerning  $\text{Fe}_3\text{O}_4\text{-ZnFe}_2\text{O}_4$  solid solution proceeds as designated by the broken line in Fig. 8.

In our experiments, the 2-3, and 4-5 samples (No. 34 and 35) contained a small

volume of  $\text{Fe}_3\text{O}_4$  (about 3~4%) in case of air cooling, and when these samples were reheated in vacuum at  $800^\circ\text{C}$ . for 2 hours, they increased the  $\text{Fe}_3\text{O}_4$  content (10~12%). But, in spite of the increase of  $\text{Fe}_3\text{O}_4$  in these samples, the intensities of the magnetization decreased remarkably from 5.8 to 0.4 as shown in Table 6. On the other hand, the intensities of magnetization of the magnetite and the solid

Table 6. Intensity of Magnetization and the Content of  $\text{Fe}_3\text{O}_4$  for various Samples.

Sample	Heated at $1250^\circ\text{C}$ . for 3 hrs. in air.		Annealed at $800^\circ\text{C}$ . for 2 hrs. in vacuum.	
	Intensity of Magnetization	Content of $\text{Fe}_3\text{O}_4$ (%)	Intensity of Magnetization	Content of $\text{Fe}_3\text{O}_4$ (%)
2-3 (No. 34)	5.8	4.2	0.6	12.3
4-5 (No. 35)	2.8	3.6	0.4	9.4
Sample	Heated at $1250^\circ\text{C}$ . for 3 hrs. in vacuum.		Annealed at $800^\circ\text{C}$ . for 2 hrs. in vacuum.	
	Intensity of Magnetization	Content of $\text{Fe}_3\text{O}_4$ (%)	Intensity of Magnetization	Content of $\text{Fe}_3\text{O}_4$ (%)
Magnetite	9.3	94	9.6	95
Solid Solution of Zinc-Ferrite and Magnetite	3.85	34	3.6	40~41.5

solution of  $\text{ZnFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  (content of  $\text{Fe}_3\text{O}_4$  is about 34%) were not decreased after the same heat treatment (annealing). These results are shown in Table 6. From these results, we ought to consider that the decrease of magnetization of annealed samples having a high  $\text{Fe}_2\text{O}_3$  content is ascribed to the eduction of the dissolved  $\text{Fe}_2\text{O}_3$ . On these facts, as has been previously mentioned, the authors consider that the ferro-magnetism of zinc-ferrite having a high  $\text{Fe}_2\text{O}_3$  contents is due to the dissolved  $\text{Fe}_2\text{O}_3$ .

## 5. Summary

Nearly 80 kinds of specimens were prepared and measurements of the electrical resistance and magnetic properties, X-ray examinations, and chemical analyses were carried out, and the following results were obtained.

1) Zinc-ferrite at a high temperature dissolves  $\text{Fe}_2\text{O}_3$  which is contained in excess over the stoichiometric amount. The maximum content of  $\text{Fe}_2\text{O}_3$  in the solid solution is about 67 mol. pct. (81.5 wt. pct.) at  $1250^\circ\text{C}$ . The compound such as  $2\text{ZnO}\cdot 3\text{Fe}_2\text{O}_3$  is nothing but a solid solution of zinc-ferrite and ferric oxide.

2)  $\text{Fe}_2\text{O}_3$  dissolved in zinc-ferrite is precipitated again by annealing.

3) It seems that the zinc-ferrite dissolves a little quantities of  $\text{ZnO}$  containing excess over the equimolar amount in the sample at high temperature.

4) Zinc-ferrite that dissolved  $\text{Fe}_2\text{O}_3$  is ferromagnetic. After annealing it is non-magnetic.

5) When zinc-ferrite contains excess  $\text{Fe}_2\text{O}_3$ , a part of  $\text{Fe}_2\text{O}_3$  is converted to  $\text{Fe}_3\text{O}_4$  by heating over  $1100^\circ\text{C}$ . in the air. On the contrary, a very limited quantity of pure  $\text{Fe}_2\text{O}_3$  is dissociated at  $1250^\circ\text{C}$ .

6) The phase diagrams for the systems  $\text{ZnO-Fe}_2\text{O}_3$  and  $\text{ZnO-FeO-Fe}_2\text{O}_3$  have been obtained by summarizing these results.

### Acknowledgments

The authors are very grateful to Dr. Hideo Nishimura for his useful suggestions in performing research work and also to the Ministry of Education for their financial support.

### References

- 1) I. Kushima and T. Amanuma: Journal of the Mining Institute of Japan. 68 (1952), 267.
- 2) H. Sawamura and A. Kosawa: Journal of the Iron and Steel Institute of Japan. 29 (1943), 307.
- 3) Y. Kato and T. Takei: Journal of the Electrochemical Society of Japan. 51 (1932), 3.
- 4) R. L. Harvey, I. J. Hegyi and H. W. Levereng: R. C. A. Review. (1950) 321.
- 5) S. Holgersson: Acta Universitatis Lundensis Lunds Universitatis Arsskrift.
- 6) M. L. Bochirol: Compts. rendus. 232 (1951), 1475.
- 7) J. Robin et J. Benard: Compts. rendus. 233 (1952), 734.
- 8) " " " " 956.
- 9) S. Iida: Shizen. 9 (1953), 40.