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## Experimental Studies on Magnetic and Crystallographic Characters of Fe-bearing Manganese Oxides

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### Abstract

In this paper are reported the interrelationships between chemical composition, Curie point, intensity of magnetization and lattice dimension of both natural and synthesized crystals in the solid-solution series  $\text{Fe}_3\text{O}_4$ - $\text{Mn}_3\text{O}_4$ .

New criterion of so-called jacobsite is proposed as well as that of mangano-jacobsite according to the magnetic and crystallographic characters of this solid-solution series.

### Introduction

Much has been investigated on natural and synthesized Mn-ferrites. VERWAY and BRUGGEN<sup>1)</sup> are the first to have synthesized ferro-manganese oxides and studied their crystallographic structure. Based upon X-ray data, they have determined the range in which  $\gamma$ -hematite is soluble in manganese tetraoxide or hausmanite,  $\text{Mn}_3\text{O}_4$ .

The discovery of Fe-bearing Mn-oxide can be dated back to 1869, when DAMOUR<sup>2)</sup> found a member of the series of solid-solution between magnetite and hausmanite in a specimen from Jacobsberg in Sweden and called it "Jacobsite". Recently MASON<sup>3)</sup> has made an investigation on this solid-solution series, and has found the range in which solid-solutions of magnetite and hausmanite can exist in different proportions.

The above-mentioned solid-solution contains what is called Mn-ferrite whose magnetism displays an anomalous phenomenon of self-reversal due to spontaneous magnetization taking place by heating the specimen. This phenomenon has been proved by NÉEL<sup>4)</sup> from a theoretical side and confirmed by GORTER<sup>5)</sup> from an experimental side, and attracts attention of many investigators interested in the Mn-containing ferrous-ferric oxides, and also those researchers NÉEL, GORTER, NAGATA, UYEDA, KAWAI and BASTA<sup>4-9)</sup> whose interests are on the geomagnetic field reversals. Quite recently by neutron diffraction experiments by HASTING and CORLISS<sup>10)</sup>, spin configuration of Mn and Fe atoms in Mn-ferrite has been clarified in detail.

On the other hand, mineralogical interest has largely been focussed upon the

occurrence of jacobsite. HIRAWATARI and MIYASHITA<sup>11)</sup> identified the Mn ore at Kiuraki mine in Kyushu as the jacobsite. And SAKURAI<sup>12)</sup> reported various localities in Japan where the minerals were found. WATANABE also referred to the occurrence of the jacobsites, especially associated with their formations.

These reports, as many are, may be said yet insufficient to explain the relations between the natural occurrence of Mn-ferrites and the magnetism of rocks containing them.

Several years ago the present writer visited Kamisugai mine, Ōsu City, Ehime Pref., Japan and there he collected a member of Mn-ore. And later on he came to find to his deep interest the fact that the ore possesses enormously strong permanent magnetism with its direction nearly parallel to the geomagnetic field *in situ*. On a later occasion the present writer's interest was doubled when he could confirm that the mineral responsible for the magnetism is the said jacobsite. Since then a study has been commenced upon the magnetic character of this mineral. The followings are the results of investigations on the Mn-ferrites having ferromagnetic character.

In part (I) is described the method by which the specimens are synthesized and in parts (II) and (III) the results of magnetic and X-ray investigations. Finally in part (IV), natural occurrence of the Mn-ferrite, and the results of the similar experimental investigations on the natural specimens.

### I. Preparation of specimen

For preparation of the specimens, the method adopted by Kawai *et al.*<sup>14)</sup> and also by Kume<sup>15)</sup> was employed as described in the following. The samples to be tested were produced by fusion of a mixture of  $Mn_3O_4$  and  $Fe_3O_4$  powder at high temperatures as described below. In the first place, pure  $Mn_3O_4$  powder was obtained by heating pure  $MnO_2$  powder at a temperature of 1250°C in air for about 4 hours. And pure powder of  $Fe_3O_4$  was prepared by heating  $\alpha$ - $Fe_2O_3$  at a temperature of 500°C in the atmosphere saturated with water vapour for about 5 hours.

Two kinds of powders thus obtained were then mixed with each other in various proportions. And each of these mixtures, after pressing tightly in the form of a cylinder, was sealed in a quartz tube whose inside air was evacuated to a pressure of  $10^{-2}$  mm-Hg.

In order to homogenize the mixture, these sealed samples were then subjected to a prolonged heating for more than 50 hours at about 1100°C. On quenching them by direct immersion into water, were obtained test specimens, whose uniform magnetic and crystallographic characters were to be tested. Each of the eight specimens thus prepared had different molecular ratios of  $Mn_3O_4/Fe_3O_4$  in percentage, 90, 84, 60, 53.3, 33.3, 24, 16.4 and 4 and was found by experiments to possess a single Curie point and to show X-ray patterns proper to a single phase. The heat-treatment mentioned above, therefore, may be considered as sufficient to produce specimens uniform in magnetic and crystallographic characters.

## II. Magnetic character of the synthesized Mn-ferrites

Since the so-called jacobsite is ferromagnetic, they must have the Curie point at which the ferromagnetism disappears. Measurements of the Curie point were made by thermo-magnetic analysis at temperatures continuously changing in a range from boiling temperature of oxygen ( $-186^{\circ}\text{C}$ ) to about  $1000^{\circ}\text{C}$ . The apparatus used (Fig. 1) is a thermo-magnetic balance of the SUCKSMITH type<sup>16)</sup>. A sample is sealed in an evacuated small quartz tube after the method of sample-sealing of Kumagai *et al.*<sup>13)</sup> and it is hung by a quartz spring at a place between and just above the truncated pole pieces of electromagnet. The intensity of magnetisation of the test specimen is obtained by measuring an elongation of the spring caused by the products of susceptibility of the specimen  $\chi$ , the magnetic field  $H$ , and the magnetic gradient there, where  $Z$  is measured in the vertically downward direction the temperature of the sample can easily be controlled by changing alternating current passing through the heating coil around the sample. Temperature dependence of the intensity of magnetization was thus obtained and the Curie point of the sample was assumed to take place at a temperature at which an abrupt decrease of the spring elongation was observed. Results of the measurements on the samples

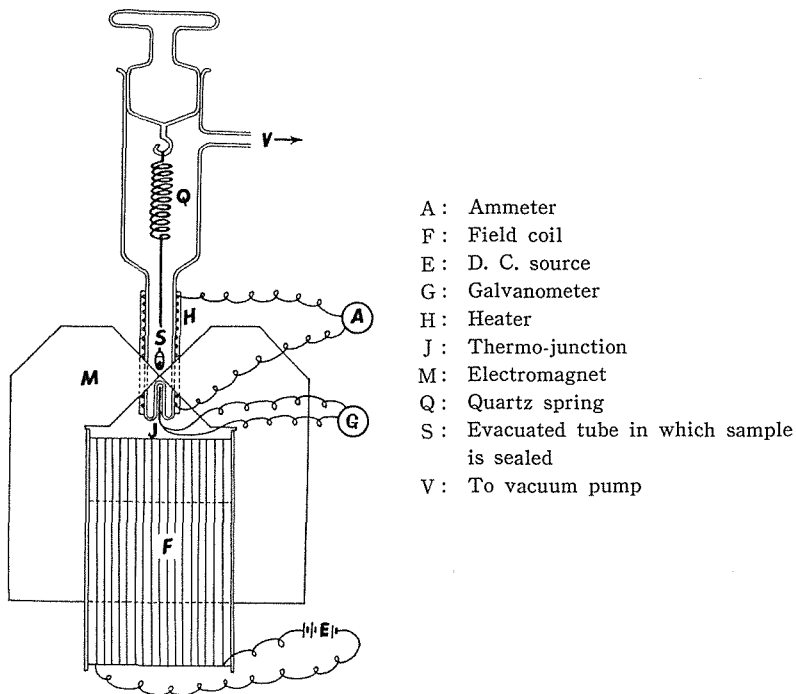


Fig. 1 Schematic diagram of thermo-magnetic balance system of SUCKSMITH type.

mentioned above show that the Curie point of the synthesized Mn-ferrites descends from that of magnetite (575°C) monotonously as Mn-content in the ferrites increases. The Curie point descends down to about 50°C when the  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio takes a value 90%. On further increasing the Mn-contents, the thermo-magnetic analysis carried out down to  $-180^\circ\text{C}$  could disclose us no Curie point. And, therefore, the specimen having the ratio greater than 90% may be assumed paramagnetic. The present writer also determined the intensity of magnetization of the specimens at the boiling temperature of oxygen  $-180^\circ\text{C}$  and under a field intensity of 10,000 Oe.

As shown in Fig. 2, intensity of magnetization of the specimens varies systematically with Mn-concentration. It is worth noticing that maximum of 140 c.g.s. e.m.u./gm. takes place at a member whose  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio is 16.7.

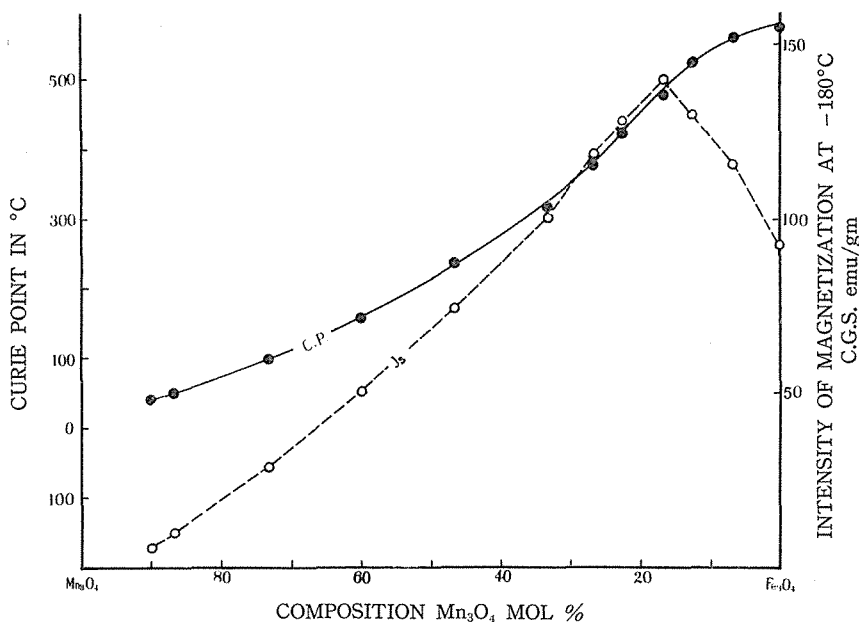


Fig. 2 Observed relations between chemical composition, Curie point and intensity of magnetization in the solid solution series  $\text{Mn}_3\text{O}_4\text{-Fe}_3\text{O}_4$ .

To be mentioned is that the maximum value of 140 c.g.s. e.m.u./gm. corresponds to about  $5.6 \mu_B/\text{molecule}$ , which is exceedingly large. So far as the present writer's observations on natural specimens of magnetite are concerned, this kind of Mn-ferrite displays the strongest intensity of magnetization, being about 1.4 times that of the pure magnetite and far stronger than any other ferrites such as Ti-, Mg- and Al-ferrites.

In March of 1958, ESCHENFELDER<sup>17)</sup> has already published a paper in which he confirms the similar maximum intensity of magnetization occurring at the  $\text{Mn}_3\text{O}_4/$

$\text{Fe}_3\text{O}_4$  ratio of 16.7% by using synthesized specimens. The present writer's result shows an astonishingly good agreement to ESCHENFELDER's result.

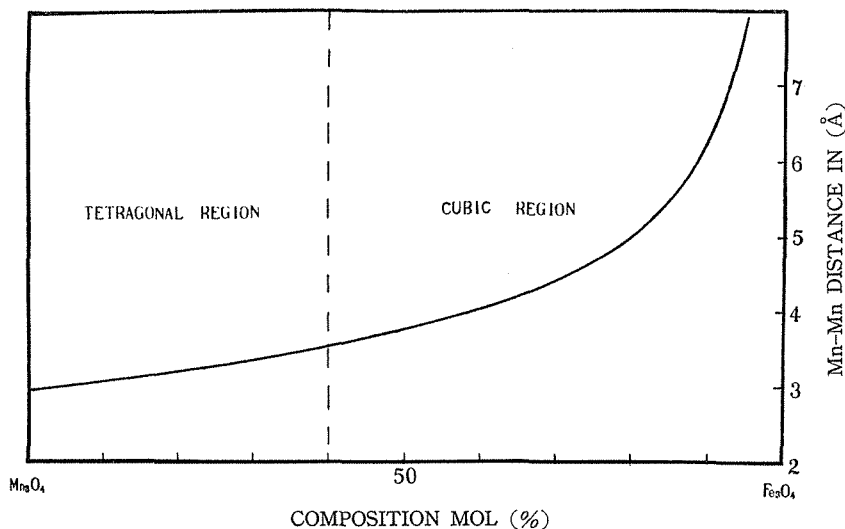


Fig. 3 Inter-ion distance of nearest Mn ions as the function of chemical composition.

### III. X-ray analysis of the synthesized Mn-ferrites

After the experiments mentioned above were finished, each of the specimens 15 in number were powdered. And for inferring crystallographic structure, ordinary DEBYE powder method was employed. Of them, those whose  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio falls between 100 and 60% show their patterns as can be indexed on the basis of tetragonal unit, whereas the rest specimens having the ratio less than 60% as can only be indexed on a basis of spinel unit of cubic symmetry. This result is shown in Fig. 4. Results of calculation of the various crystallographic parameters, axial units, the ratio  $c/a$  etc, are given in Tables I, II and III.

From Fig. 4 it is very clear that the hausmanite-magnetite series can be divided into two sub-series, one having tetragonal structure and composition ranging from that of hausmanite to 60% of  $\text{Mn}_3\text{O}_4$ , and the other cubic and ranging from this composition to that of magnetite. For convenience' sake, let us tentatively call the tetragonal phase "mangano-jacobsite". As shown in Fig. 3 the change of the lattice dimension with respect to chemical composition, is continuous when we pass through the point of 60% of  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  where tetragonal lattice-arrangement changes to cubic. This is consistent with the VEGARD's law on the continuous solid solution.

Table I. Tetragonal-type crystallographic structure in  $\text{Mn}_3\text{O}_4\text{-Fe}_3\text{O}_4$  Series.  
 $\text{FeK}=1.9373\text{\AA}$  Camera radius 50.37 mm

G. Aminoff (1926)			I. Yun (1958)				G. Aminoff (1926)			I. Yun (1958)			
$\text{Mn}_3\text{O}_4$			$\text{Mn}_3\text{O}_4$ (100%)		$\text{Mn}_3\text{O}_4$ (84%)		$\text{Mn}_3\text{O}_4$			$\text{Mn}_3\text{O}_4$ (100%)		$\text{Mn}_3\text{O}_4$ (84%)	
hk1	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I	hk1	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I
101	0.156	w					321	1.508	m	1.506	5	1.447	5
112	0.392	m	0.397	3	0.416	5	224	1.576	st	1.579	8	1.614	8
200	0.452	w					400	1.808	m	1.710	6	1.862	7
103	0.492	st	0.493	9	0.511	10	305	2.068	w(-)	2.035	1	2.021	2
211	0.604	st	0.608	10	0.587	8	413	2.300	w(+)	2.292	2	2.352	2
004	0.672	m					404	2.480	w(+)	2.469	2	2.478	3
220	0.904	m	0.903	4	0.863	3	127	2.628	w				
204	1.124	w(-)	1.145	1	1.132	1	008	2.696	w	2.743	1	2.742	2
105	1.164	m	1.156	3			415	2.972	m	2.969	3	3.010	3
312	1.300	w	1.300	2	1.277	2	521	3.316	m	3.219	4	3.220	4
303	1.396	w	1.356	9	1.352	9							

Table II. Cubic-type crystallographic structure in  $\text{Mn}_3\text{O}_4\text{-Fe}_3\text{O}_4$  Series.  
 $\text{FeK}=1.9373\text{\AA}$  Camera radius 50.37 mm

I. Yun (1958)												
hk1	$\text{Mn}_3\text{O}_4$ (4%)		$\text{Mn}_3\text{O}_4$ (16.7%)		$\text{Mn}_3\text{O}_4$ (24%)		$\text{Mn}_3\text{O}_4$ (33.3%)		$\text{Mn}_3\text{O}_4$ (53.3%)		$\text{Mn}_3\text{O}_4$ (60%)	
hk1	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I	$4 \sin^2$	I
220	0.4240	7	0.4225	7	0.4165	7	0.4147	7	0.4105	7	0.4080	7
311	0.5899	10	0.5829	10	0.5731	10	0.5730	10	0.5646	10	0.5609	10
222	0.6386	2	0.6339	2	0.6241	2	0.6224	2	0.6166	2	0.6142	2
400	0.8528	8	0.8462	8	0.8301	8	0.8287	8	0.8221	8	0.8165	8
420	1.1066	3										
422	1.2757	4	1.2589	4	1.2443	4	1.2427	4	1.2330	4	1.2251	4
333	1.5524	8	1.4370	8	1.3980	8	1.3953	8	1.3897	8	1.3855	8
400	1.7004	9	1.6791	9	1.6556	9	1.6538	9	1.6435	9	1.6420	9
531	1.8762	1	1.8448	1	1.8129	1	1.8011	1	1.7973	1	1.7908	1
620	2.1215	2	2.0989	2	2.0762	2	2.0681	2	2.0432	2	2.0301	2
533	2.2772	5	2.2518	5	2.2276	5	2.2243	5	2.2102	5	2.2086	
622	2.3307	1	2.3071	1	2.2853	1		1	2.2582	1		
444	2.5244	3	2.5188	3	2.4895	3	2.4827	3	2.4698	3	2.4660	3
642	2.9772	6	2.9307	6	2.9032	6	2.8978	6	2.8861	6	2.8832	6
553	3.1347	8	3.1092	8	3.0574	8	3.0504	8	3.0425	8	3.0378	8
800	3.3956	7	3.3738	7	3.3270	7	3.3073	7	3.2918	7	2.2882	7

Table III. Variation of lattice dimensions and Curie point  
in  $Mn_3O_4$ - $Fe_3O_4$  series.

Mol. % $Mn_3O_4$	Tetragonal			Cubic						
	100	84	73.3	60	53.3	33.3	24	16.7	4	0
Lattice Dimension in (Å)	a = 8.116	8.235	8.445	8.620	8.549	8.516	8.500	8.450	8.412	8.39
	c = 9.426	9.227	8.950							
Curie point in (°C)	—	60	100	160	240	320	380	480	560	573

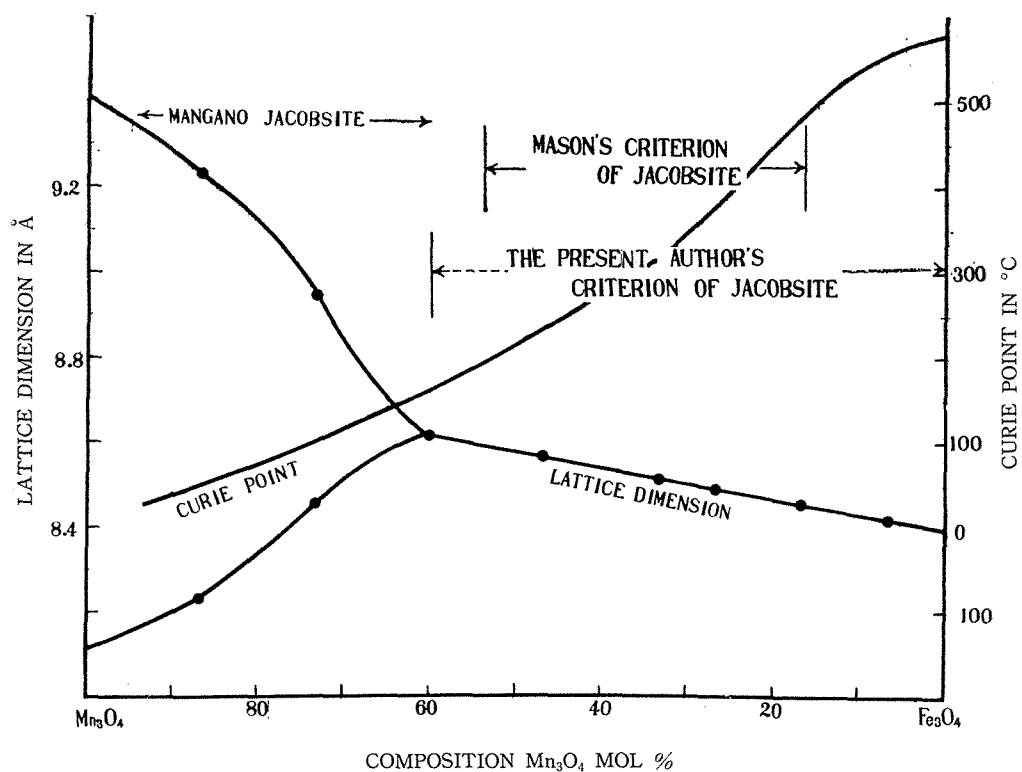


Fig. 4 Observed relations between chemical composition, Curie point and lattice dimension. The new criterion of jacobsite proposed by the present author is also shown on the same diagram.



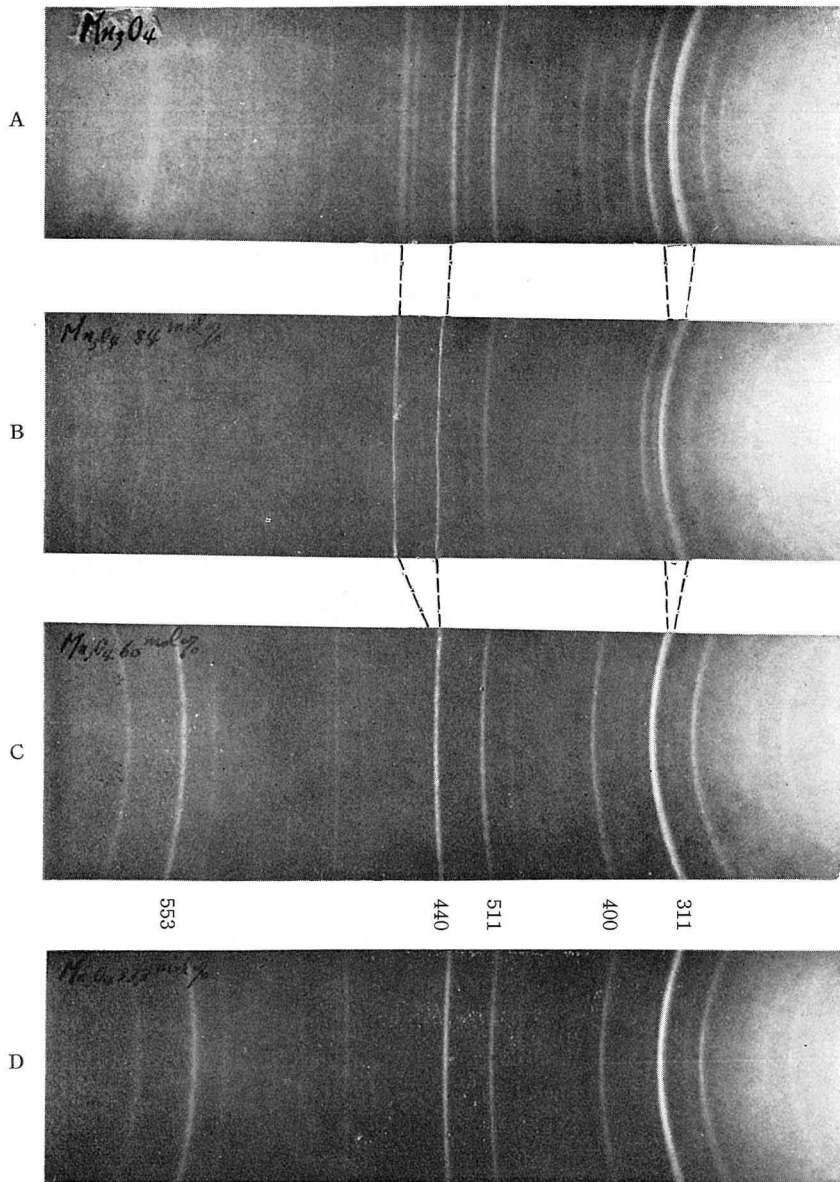


Fig. 5 X-ray powder patterns in which are shown the splitting of  $\begin{pmatrix} 311 \\ 440 \end{pmatrix}$  lines of cubic phase into  $\begin{pmatrix} 103 \\ 224 \end{pmatrix}$  and  $\begin{pmatrix} 211 \\ 400 \end{pmatrix}$  lines of tetragonal, as  $Mn_3O_4$  composition passes through 60% in increasing sense  $Mn_3O_4/Fe_3O_4$ .  
 A: 100%, B: 84%, C: 60%, D: 16.7%.

MASON<sup>3)</sup> has given a name "Jacobsite" to the ferromagnetic Mn-ferrite whose composition is in the range from 54 to 16.7% of  $Mn_3O_4$  concentration. The Curie points of the two end minerals of this range are, according to the present study, 160° and 480°C respectively (Fig. 4). However, as will be described later in item 2 of Part IV, Mn-ferrites whose composition are outside the MASON's criterion and whose magnetism resembles that of the jacobsite after MASON's criterion, can be found frequently in natural ores. For an instance, a Mn-ferrite whose  $Mn_3O_4$  composition is 60% and exceeds 54%, the higher extremity of MASON's criterion occurs in nature.

Another example is a mineral having the  $Mn_3O_4$  composition less than 16.7%. This mineral is also abundant in the so-called natural magnetite and possesses magnetic character different from that of pure magnetite.

The present writer proposes, therefore, that it will be plausible that the MASON's criterion should be extended in two directions, such that the lower extremity of criterion should take a value of 0% of  $Mn_3O_4$  and the higher 60%. According to this new proposal, the name jacobsite should be given to the Mn-ferrites falling between these two limiting compositions of  $Mn_3O_4$ . In the Fig. 4, are represented the transition of crystal structure from cubic to tetragonal phase through the point of 60% of  $Mn_3O_4$  composition. We can recognize the splitting of the  $\begin{pmatrix} 311 \\ 440 \end{pmatrix}$  line of cubic phase into the doublets  $\begin{pmatrix} 103 \\ 224 \end{pmatrix}$  and  $\begin{pmatrix} 211 \\ 400 \end{pmatrix}$  of tetragonal phase.

In connection with this crystallographic transition, some abrupt changes are expected to occur in magnetic behaviour as are often the case with many magnetic materials. However, as clearly shown in Figs. 3 and 4, this expectation fails, as both the curves showing Curie point  $J_s$  are very smoothly changing in the vicinity of 60% composition of  $Mn_3O_4$ . Therefore, this fact seems to be peculiar.

#### IV. Jacobsite occurring in nature

Thermo-magnetic observations have been carried out on more than 50 natural specimens of the so-called manganese ores such as polianite, brownite, hausmanite, rhodochrosite, rhodonite etc. The results of observations have shown that most of these natural samples, regardless of difference in localities from which they were taken, possess ferromagnetic phases although they are not so much. The X-ray analyses on the ferromagnetic powder specimens which were picked out by magnetic separation have been carried out. The results have shown that the said phases are nothing but what we have defined as jacobsite in the preceding section by a criterion wider than MASON's one.

It is also found from thermo-magnetic analyses that these jacobsites are occasionally of double or triple phases. In such a case there appear on the thermo-

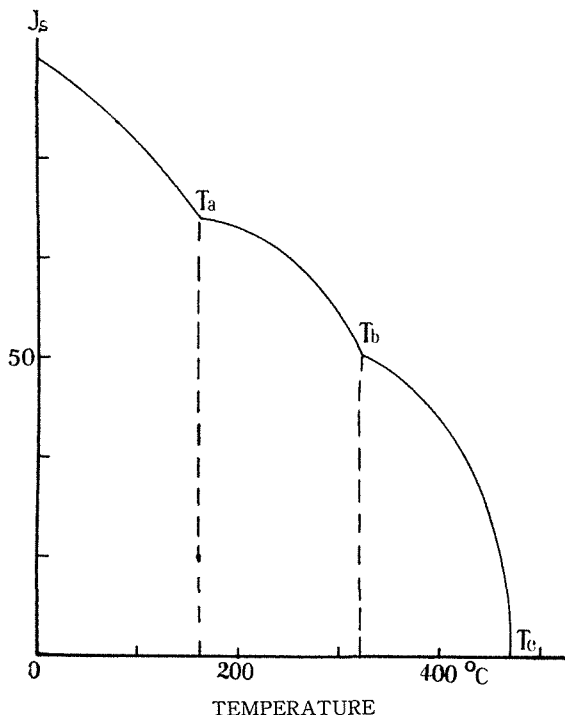


Fig. 6 Temperature dependence of intensity of magnetization of a natural specimen having three phases.

magnetic curve sharp fallings or knicks at different temperatures. One of the representative example is shown by Fig. 6, the three observed Curie points ( $T_a$ ,  $T_b$ ,  $T_c$ ) in the figure show the co-existence of different phases with different compositions.

By taking 50 samples of natural jacobites, frequency of Curie point was determined by thermo-magnetic analysis. The results are shown in Fig. 7, in which the abscissa of chemical composition is also represented.

As is easily recognizable in the figure, a remarkable maximum frequency occurs at the Curie point  $160^\circ\text{C}$ , to which corresponds the content of 60%  $\text{Mn}_3\text{O}_4$ . This fact implies that the ferromagnetic spinel having this  $\text{Mn}_3\text{O}_4$  content. Mn-ferrite appearing most frequently in nature is that the transient mineral between spinel and tetragonal Mn-ferrites.

Next, separation into single phase by means of magnetic separator was carried out with samples from Taga and Kitchō mines, Kyoto Pref., Kaso mine, Tochigi Pref., and Kamisugai mine, Ehime Pref., Japan. The single ferromagnetic phases thus obtained are then subjected to both the thermo-magnetic and the X-ray analyses.

The results indicate that variation of Curie point of these single phases speci-

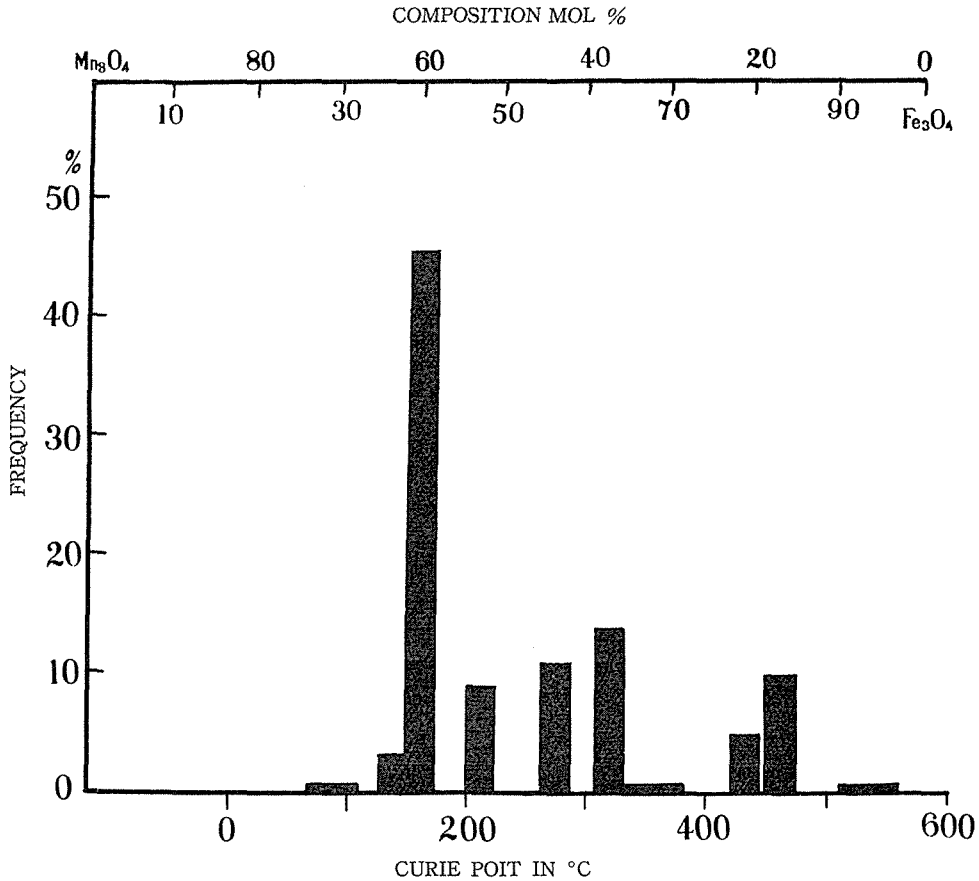


Fig. 7 Histogrammatic representation of Curie point frequency in natural specimen of Mn-ferrites.

mens with respect to lattice constant shows a fair agreement to the similar variation which have been already obtained with synthesized samples. The results are plotted in Fig. 8, in which the two continuous curves are those determined with synthesized samples.

In Fig. 8 are also plotted two data of natural samples, one from Jacobsberg, Sweden<sup>18)</sup> and the other from Tamworth, N.S.W.<sup>19)</sup>. These two data are coordinated by Curie point determinations and chemical analysis.

The coordination of this six points plotted in Fig. 8 indicates that these natural specimens of single phase are precisely identical with the synthesized specimens.

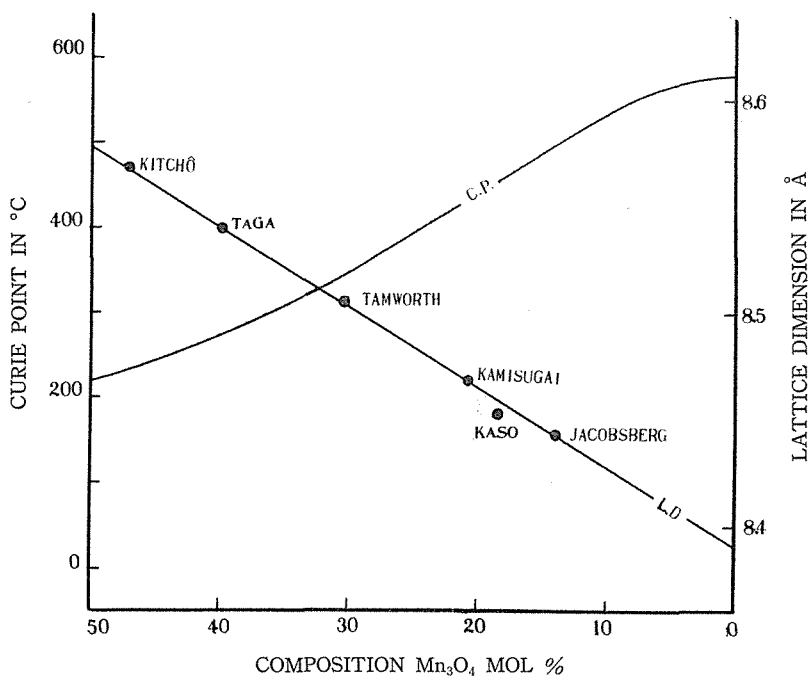


Fig. 8 Relations of Curie point and lattice dimension to chemical composition in natural specimens of jacobsite of single phase.

### V. Conclusion

We can summarize the preceding results in the following items:

1) Two kinds of solid-solutions of  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  have been experimentally confirmed. Of them one is the mangano-jacobsite solid-solution having tetragonal crystallographic structure; the members of this solid-solution having  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio from 60 to 90% at least is ferromagnetic and those from at least 90 to 100% probably para-magnetic. The other is the jacobsite solid-solution having cubic crystallographic structure; members of this solid-solution have  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio ranging from 60 to 0%, and all of these members are also ferromagnetic.

2) Curie point *vs* composition relations in both the two solid-solutions have been established.

3) MASON's original criterion of jacobsite has been extended by the present writer to a wider criterion defined by the range from 0 to 60% of  $\text{Mn}_3\text{O}_4$ .

4) On the intensity of magnetization of jacobsite, a special note should be given here. Namely,  $J_s$  of a jacobsite whose  $\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$  ratio is about 16.7% has an exceedingly high maximum value of 140 c.g.s. e.m.u./gm, which is consistent with ESCHENFELDER's result. This maximum value is equal to about  $5.6 \mu_B$ /molecule and to about 1.5 times  $J_s$  value of a pure magnetite.

5) As described above, jacobsite possesses very strong remanent magnetism due to its ferromagnetic character. This suggests that magnetic prospecting may be applicable to the manganese ore deposit associated with Mn-ferrite, and this has been overlooked up to date.

6) By utilizing this behavior of ferromagnetism, a magnetic separation of Mn-ferrite ore having enriched content of Mn from a mixture of ores of higher and lower grades is possible. There are two ways of the magnetic separation:

a) Utilization of the difference in intensity of magnetization.

Changing the intensity of a magnetic field applied to the pulverized Mn-ferrite ore, one can collect into groups the various kinds of pulverized ores with nearly constant Mn-contents, because of the difference in intensity of magnetization of pulverized ores.

b) Utilization of the difference in Curie point.

If we heat the pulverized ores to a temperature over one of the Curie points of the  $Mn_3O_4$ - $Fe_3O_4$  solid solution series, those pulverized ores having their Curie points lower than this Curie point can be magnetically separated from those having higher Curie points.

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