Phase Transition of Li_2O—Fe_2O_3 System. I. Thermal and Electric Properties of Lithium Ferrite $LiFeO_2$

By Eizo KATO

(Received September 2, 1957)

In 1931, Posnjak and Barth⁽¹⁾ interpreted an X-ray diffraction pattern obtained from an isometric modification of lithium ferrite, and found that its crystal structure is of sodium chloride type, O_h^5–$Fm3m$, in which cations, lithium and ferric ions, are randomly distributed among the equivalent points. This crystal has variate atom equipoint structure. At the same time they observed that lithium ferrite has an anisotropic modification below about 600°, but did not explain the relation between these two modifications. For the cubic modification Kordes⁽²⁾, Hoffmann⁽³⁾ and Collongues and Chaudron⁽⁴⁾ gave the lattice constants.

In 1944, Barblan et al.⁽⁵⁾ showed that unknown anisotropic modification is tetragonal, D_{4h}^{19}–$I4/amd$, in which lithium and ferric ions are arranged in the different equivalent positions, and that the phase transition between these modifications is an order-disorder one. In addition, they stated that the modifications sluggishly transform within 570–670°. Recently Collongues⁽⁶⁾ found that another orderd modification exists at the temperature range below the preceding ordered phase. These investigations were made only by X-ray diffraction method and the transition temperature was vague.

The author was interested in the correlation between the crystal structure and

---

1) E. Posnjak and T. F. W. Barth, *Phys. Rev.*, **38**, 2234 (1931).

2) E. Kordes, *Z. Kryst.*, **92**, 139 (1935).

3) A. Hoffmann, *Naturwiss.*, **26**, 431 (1938).

4) R. Collongues and G. Chaudron, *Compt. rend.*, **231**, 143 (1950).

5) F. Barblan, E, Brandenberger and P. Niggli, *Helv. Chim. Acta*, **27**, 88 (1944).

6) R. Collongues, *Compt. rend.*, **241**, 1577 (1955); *Bull. soc., chim. France*, **1957**, 261.

the physico-chemical properties in the course of transition, and measured the the thermal electric properties of lithium ferrite.

Experimental

i) **Specimens.**—Ferrous oxalate and lithium corbonate were mixed in wet condition and heated in an open furnace at ca. 800° for a day. In order to complete the reaction, the above procedure was repeated with an excess of lithium carbonate, which was removed by cold dilute acetic acid.

Anal. Found: Li_2O, 15.73 %; Fe_2O_3, 82.00 %; insoluble, 0.33 %. Calcd. for $LiFeO_2$: Li_2O, 15.76 %; Fe_2O_3, 84.24 %.

Ceramic specimens to be tested were prepared according to Weisz[7], i. e., fine-ground powder of the products was mixed with a little quantity of triethanolamine stearate and of *Carbowax 3000* as binder and lubricant, and then moulded with a pressure of 100 kg./cm^2. After being sintered at ca. 1000° for two hours, they were further given appropriate heat treatments; ordered specimens were annealed at ca. 570° for more than fifty hours, and disordered specimens were quenched by rapid cooling, either by immersion into water or exclusion of the air.

The specimen for dilatometry was rod-shaped, 7 mm. in diameter and 5 cm. in length. For electric measurement a pellet was prepared, 1 cm. in diameter and 2~5 mm. in thickness. Both sides of the pellet were polished with emery powder.

For the identification of these specimens, X-ray powder diffraction method was taken with Fe$K\alpha$ radiation. The observed lattice constants showed the following values and agreed with former investigators',

ordered phase: $a=4.034$ Å, $c=8.71$ Å;
disordered phase: $a=4.145$ Å.

ii) **Apparatus and Procedures.**—Sudo's apparatus[8] was used for differential thermal analysis, which was made by Mitamura & Co. Ltd. The nickel vessel has three holes; the outside one was packed with alumina powder as standard and the opposite one by fine-powdered probe. The temperature difference between these two materials was measured by means of an inserted platinum-platinum rhodium themocouple connected to a galvanometer. The mid hole contained alumina, in which another thermocouple was inserted to measure the temperature of the whole assembly. The ascending rate of temperature in the furnace was manually controlled. The apparatus was not appropriate for a sluggish transition, because it was constructed for a mineralogical investigation for a comparatively rapid rate of temperature rises so that the measurement at slower rate than 0.4°/min. was impossible.

The schematic diagram of dilatometer is shown in Fig. 1. The difference of thermal expansion between the specimen and a quartz glass was observed by mirror-telescope-scale system. The temperature was measured with a Chromel-Alumel thermocouple, which was inserted near the specimen and connected to a Potentiometer Type K-2 Shimadzu Seisakusho Ltd. The reading of elongation had an accuracy of ca. 7×10^{-6} cm. and the reading of temperature of ±0.1°. To adjust the heating rate, the temperature of the furnace was controlled with a Potentiometer-type

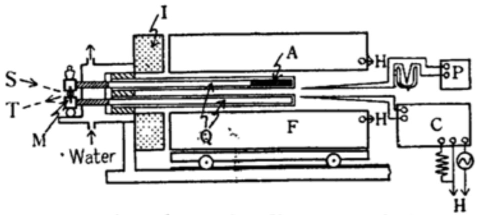

Fig. 1. A schematic diagram of dilatometer.

A: specimen to be tested;
C; temperature controller;
F: furnace;
I: heat-insulating ceramics, "Isolite N-4";
M: mirror;
P: potentiometer;
Q: quartz glass rod;
S: scale;
T: telescope.

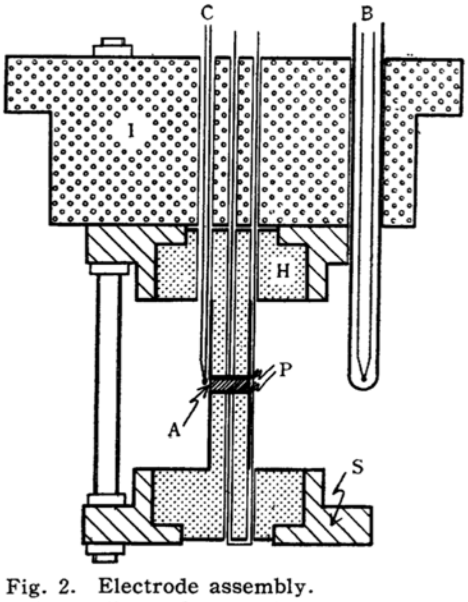

Fig. 2. Electrode assembly.

A: pellet to be tested;
B: Pt-PtRh thermocouple;
C: Chromel-Alumel thermocouple;
H: sillimanite holder;
I: heat-insulating ceramics, "Isolite N-4";
P: Pt foil;
S: heat-resistant steel.

---

[7] R. S. Weisz, *Ceram. Ind.*, **58**, No. 4, 130, 133; No. 5, 76 (1952).

[8] Toshio Sudo, "The Clay Minerals (Nendo-kobutsu)", Iwanami Shoten, Tokyo, 1953, p. 49.

Controller Chino Works Ltd., which permits the fluctuation of ±1°.

D. C. resistance was measured with a D. C. Bridge Type BR-7A Shimadzu Seisakusho Ltd. Electrode assembly* is shown in Fig. 2. The pellet was placed between two discs of platinum foils to which lead wires were attached. The platinum foils and the pellet were tightly fitted by steel holders to ensure a good contact. All the assembly except the upper-insulating part was inserted in a vertical furnace, and the resistance was measured as a function of temperature.

The bridge was connected to two volt d. c. source, thus the pellet was placed in a constant electric field during the measurements. The resistance at room temperature was measured with Megger Type L-4 Yokogawa Electric Works Ltd., because it was too large to be measured with a bridge. Determination and control of temperature were by the same method as in the case of the dilatometry.

Results and Discussion

Differential Thermal Analysis. — In general, there is a change in specific heat with phase transition. For an exact study of the transition, it is desirable to measure the specific heat at various temperatures. However, for the sake of simplicity, the differential thermal analysis was adopted to see the transition.

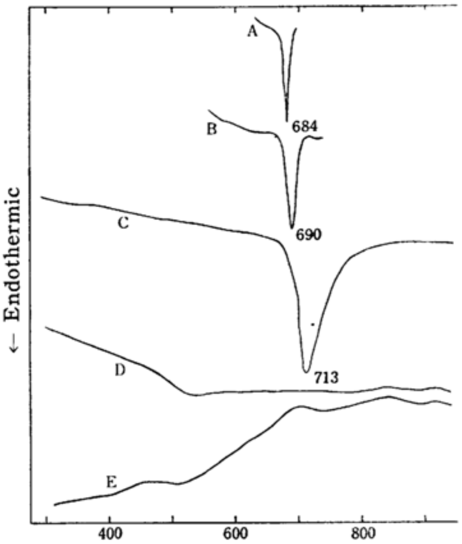

Fig. 3. Differential thermal analysis of $LiFeO_2$.
- A: annealed at 570° for 50 hr., repeated twice: 0.4°/min.;
- B: annealed at 570° for 60 hr.: 1.6°/min.;
- C: same as B: 10°/min.:
- D: annealed at intervals of 100° from 1000° to 500° for 12 hr. at each temperature: 10°/min.;
- E: quenched from 1000° in the air: 10°/min.

Since it is obvious that the transition velocity is very sluggish, a series of thermal analyses under various conditions were performed. The deflection of the galvanometer as a function of temperature is shown in Fig. 3. The curves A and B are registered with a different scale from the curves C, D and E, for the deflection of the former is smaller than that of the latter owing to the slow rise of temperature.

The curves, measured under various rates of heating for ordered specimens, are A, B and C. The endothermic reaction evidently appears in each case, and the corresponding temperatures are 684°, 690° and 713° for the curves A, B and C, respectively. It is well known that the endothermic reaction appears by the phase transition between the stable modifications. To verify this phenomenon, the curve E was taken using a disordered specimen. In the commenting temperature range no reaction is observed on the curve. Undoubtedly this reaction can be attributed to the order-disorder transition.

Considering the following two points, it is confirmed that the transition velocity is very sluggish. First, it is difficult to obtain perfect ordered specimens, in spite of annealing for a considerably long time, as is obvious in the specimen for curve D. Secondly, difference in endothermic temperatures is caused by the difference in heating rate among the curves A, B and C. If it were measured at a slower rate than 0.4°/min., it could be expected to settle down to a definite temperature which is somewhat lower than 684°; this is impossible with our apparatus.

Dilatometry.—By measurement of the linear coefficients of thermal expansion with a heating rates both for annealed and quenched specimens, Fig. 4 was obtained.

The expansion coefficient is remains unchanged at 300° to 750°C (1.80×10^{-5}), for the ordered specimen at a heating rate of 30°/hr. The same result is obtained at as rate 5°/hr. The anomaly of expansion distingushably appears when the heating rate is brought down to 2°/hr. For the purpose of verifying the behavior around the transition temperature, the expansion curve measured at rate of 1°/hr. is shown

---

[*] The author was referred to Parravano's apparatus; G. Parravano, *J. Chem. Phys.*, **23**, 5 (1955).

in Fig. 5, where the expansion coefficient becomes maximum at 660±2°. The increment caused by the anomalous expansion for this case is 0.12 %.

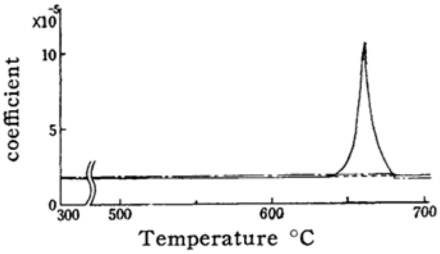

Fig. 4. Curves of expansion coefficient *vs.* temperature of $LiFeO_2$.
——: ordered specimen: 1°/hr. above 550°, 30°/hr. below 550°;
- - -: above specimen at 30°/hr. within the anomalous range;
—·-: disordered specimen: 80°/hr.

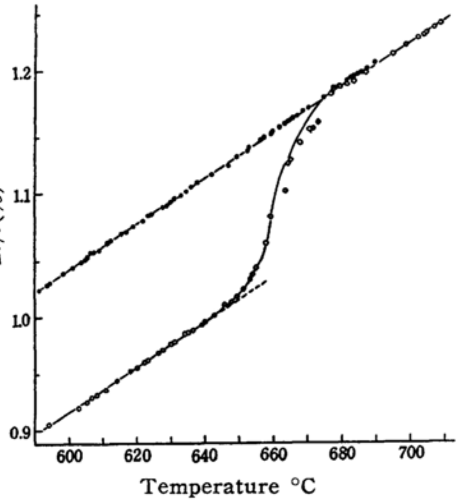

Fig. 5. Expansion curves of ordered specimen around the transition temperature.
○: ascending;
●: descending.

The descending curve is measured down to 550° with the same specimen at a rate of 1°/hr. and a constant coefficient 1.85×10^{-5} is obtained. Although it shows an irreversible process as in a monotropic transition, this is due to the long time required by this transition. The same sort of measurement was carried out for the quenched disordered specimens. Their coefficients were 1.88×10^{-5} below and 1.61×10^{-5} above 680°C at considerably rapid ascending rate. From these results, the transition temperature is determined to 660±2°, inferred to the results of differential thermal analysis.

Electric Resistance Measurement.— Electric properties in relation to the phase transition are generally studied by the measurement of dielectric constant and dielectric loss. The electric resistance of our pellets is not great enough at higher temperatures, to enable their measurement. It may be natural that a strict reproducibility can not be expected for the measurement of electric resistance of a semiconductor. It is, therefore, necessary to repeat the same sort of measurement. In fact, it is quite difficult not only to make each resistance-temperature curve coincide, but also to determine the transition temperature in which the anomalies appear. From more than twenty measurements, some significiant examples are shown in Fig. 6. Generally, the curves similar to A are observed at a rapid heating rate (30°/hr.), and the curves similar to D, at a slower rate (2°/hr.). The tangent of ρ versus $1/T$ steadily decreases in the former, while the change of the tangent is found within 660–680° in the latter. A peculiar example is the curve B, in which a negative tangent is observed in the above temperature range. The pellet was placed in a steady electric field during the measurement; electrolysis was indicated on the pellet surface. The circuit was kept closed for as short a time as possible to obtain a reading of the curve C, in order to minimize the influence of electrolytic polarization. An anomaly of electric resistance is recognised within 660–680° from these results.

A semiconducting feature is expressed by

$$\rho=\rho_0\exp(-\phi/\boldsymbol{k}T),$$

where ρ : electric resistance
ρ_0: constant
ϕ : activation energy
$\boldsymbol{k}$: Boltzmann constant
T: absolute temperature

From the above results, the values of activation energy are 0.65∼0.9 eV for ordered specimen (200∼400°), 0.3 eV for disordered specimen (100∼300°) and 1.2∼1.4 eV for each specimen (680∼710°). The net resistance at room temperature has the order of magnitude 1000 MΩ for ordered specimens and several MΩ for disordered ones.

When the current has flowed for a long time, color change is observed on the surface; the cathode side is white and the opposite is brown, At the same time, white materials which contain lithium adhere to platinum cathode. Those color

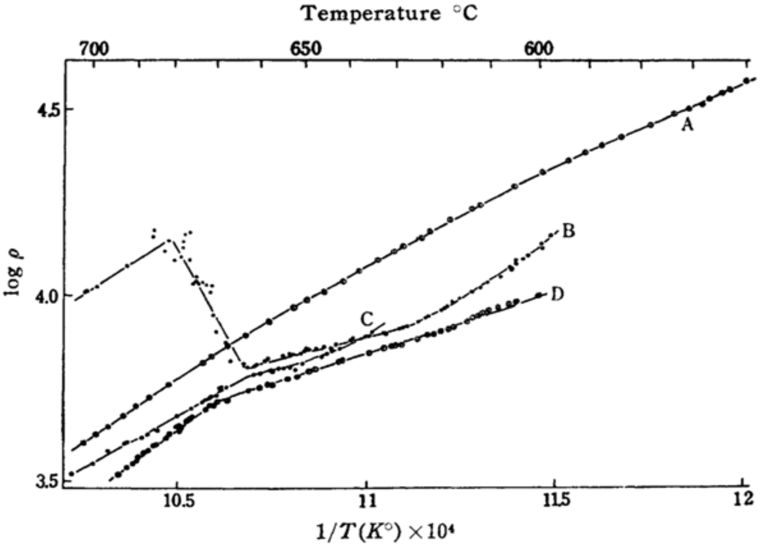

Fig. 6. D. C. resistance curves of $LiFeO_2$.

changes are hard to find below 300°, and become more evident with increasing temperature. For the materials having the order-disorder transition such as AgI and Ag_2HgI_4, it is known that the conduction is electrolytic, owing to the vacant points in the lattice. The conduction mechanism is also electronic for the material containing iron such as magnetite. From the above simple experiment, considering the influence of excess of Li_2O, it is assumed that the electrolytic conduction takes place within the temperature range of transition.

Summary

The measurements of differential thermal analysis, thermal expansion and d. c. electric resistance for lithium ferrite were performed in relation to the order-disorder transition. Conclusions are described as follows;

(1) The endothermic reaction and the anomalous expantion take place during the transition.

(2) The value of the transition temperature is determined as 660±2°C. by means of dilatometry.

(3) The existence of electrolytic conduction is qualitatively recognized.

(4) It is verified that the transition is very sluggish.

The author wishes to express his sincere thanks to Professor S. Nagaura of Osaka City University for his kind advice and encouragement during this work.

The Institute of Polytechnics
Osaka City University
Kita-ku, Osaka