*Phase Transition of $Li_2O—Fe_2O_3$ System. II. Thermal and Electric Properties of Lithium Ferrospinel $LiFe_5O_8$**

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Lithium ferrospinel has been used as magnetic material for high frequency field because of its ferromagnetic properties. The ferrimagnetism for lithium ferrospinel and other ferrites was widely studied; Weisz1) gave a detailed review concerning its practical uses.

In 1938, Hoffmann2) studied the crystal structure of lithium ferrospinel by means of X-ray diffraction method. He found that its crystal structure is spinel-type, O_h^7-$Fd3m$. After Hoffmann's work Barblan3), Collongues4) and Kordes5) investigated the same problem and determined the lattice constant. All of these investigators confirmed the structure of disordered modification, that is, the lithium and the ferric ions in octahedral positions are distributed at random.

In 1949, Braun6) investigated the extra-line of lithium ferrospinel, which could not be explained by spinel structure, and determined the space group of its ordered modification, O^6—$P4_33$, in which lithium and ferric ions in octahedral positions are arranged in different positions. The transition was observed at 735° to 755°C. Verwey et al.7) calculated the contribution of long-range ordering to lattice energy using the above-mentioned structures. It is worth mentioning that Behar8) clarified the mechanism of the order-disorder transition of lithium ferrospinel by metallurgical technique.

In the following sections of this paper the thermal and the electric properties of lithium ferrospinel will be described from the viewpoint of order-disorder transition, and the correlation between lithium ferrite and lithium ferrospinel will also be discussed.

Experimentals

Specimens.—Lithium ferrospinel was prepared by a similar method to that for lithium ferrite; only heat treatments will be described here. An ordered specimen can be satisfactorily obtained by annealing in a furnace from ca. 800° to the room temperature, while a disordered specimen by rapid cooling, immersed into water from 1000°. The lithium content in the specimens was analysed by means of flame photometry; Found: 3.09%, Calcd. for $LiFe_5O_8$: 3.61%.

For the identification of the above specimens, X-ray diffraction was carefully applied by the back-reflection method, and the following observed values of lattice constant agreed with former investigators';

ordered phase; $a=8.329_6\pm0.000_5$ Å,
disordered phase; $a=8.332_6\pm0.000_5$ Å.

Apparatus and Procedure.—The apparatus used for differential thermal anlysis, dilatometry and d.c. electric resistance measurements are all the same as were described in the previous paper; no further description will be given.

Results

Differential Thermal Analysis. — A series of differential thermal analyses under various heating rates were performed, to obtain preliminaly knowledge for further measurements concerning the transition temperature and the transition velocity. The resultant curves are shown in Fig. 1, where the curves A and B are registered with a different scale from that of other curves, corresponding to the different heating rate, to exaggerate the relatively small effect. Some features of these curves are as follows:

(a) For the ordered specimens well-annealed, the apparent temperatures of endothermic reaction seem to converge from 766° to 745.5° according as the rate is slower. No wide spreading of apparent

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* *Lithium ferrospinel* stands for $LiFe_5O_8$, to avoid confusin with $LiFeO_2$ of sodium chloride structure.

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

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

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

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

5) E. Kordes and E. Röttig, *Z. anorg. allgem. Chem.*, **264**, 34 (1951).

6) P. B. Braun, Paper at ASXRED meeting, Itheca, 1949; *Nature*, **170**, 1123 (1952).

7) F. de Boer, J. H. van Santen and E. J. W. Verwey *J. Chem. Phys.*, **18**, 1032 (1950); E. J. W. Verwey, P. B. Braun, E. W. Gorter, F. C. Romijn and J. H. van Santen, *Z. Phys. Chem.*, **198**, 6 (1951).

8) I. Behar, *Compt. rend.*, **242**, 2465 (1956).

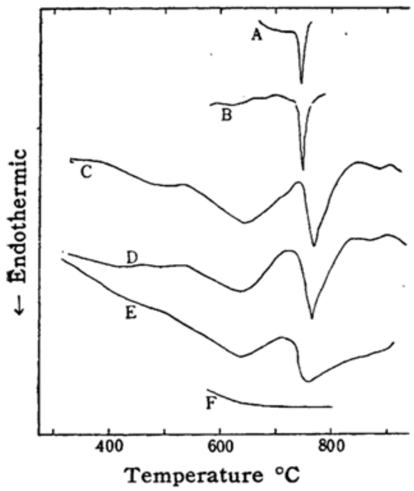

Fig. 1. Differential thermal analysis of $LiFe_5O_8$.

- A: annealed in a furnace after being cooled from 850° to 580° at 30°/hr.: 0.5°/min.;
- B: same as A: 1.5°/min.;
- C: annealed at intervals of 100° from 1000° to 500° for 12 hrs. at each temperature: 10°/min.;
- D: quenched from 1000° in the air: 10°/min.;
- E: quenched from 1000° in water: 10°/min.;
- F: quenched from 1000° in water most rapidly: 1.5°/min.

transition temperatures, as in the case of $LiFeO_2$, was obtained (Curves A, B and C).

(b) The curve F is that for a disordered specimen, quenched as rapidly as possible, and shows no reaction at 700—800° different from other. It may be concluded that the endothermic reaction around 745.5° is due to the order-disorder transition.

(c) Another endothermic valley is found at 635—638° (Curves C, D and E).

(d) The curves change from A to F, as the specimen transfers from ordered to disordered form. By comparison of the curves D, E and F, it is seen that the quenching must be completed within 1~2 seconds for the preparation of the disordered specimen. As for the curve E for the semi-ordered specimen, the endothermic deflection due to the transition is somewhat smaller than that of the ordered specimen.

Dilatometry. — Thermal expansion of ordered and disordered specimens was measured, in order to confirm the transition temperature taken from the differential thermal analysis and to know the volume change caused by the transition. Linear expansion coefficients as a function of the temperature are shown in Fig. 2. Since the transition velocity gets extremely low around the transition temperature, at the lower temperature range it is not the case, the measurements at different temperature ranges were undertaken under different ascending rates, e.g. 100°/hr. for 400—570°, 30°/hr. for 570—680° and 5°/hr. for above 680°. The curve of a quenched specimen which was obtained at the rate of 100°/hr. has much complexity. It is not only difficult but seems meaningless to make a detailed analysis of the curve. The negative coefficient at 700—800°, however, is probably due to the ordering from disordered phase. From these curves, it is seen that the transition occurs at

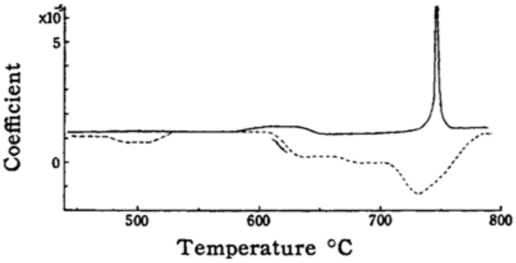

Fig. 2. Curves of expansion coefficient vs. temperature of $LiFe_5O_8$.
——: ordered specimen;
------: disordered specimen.

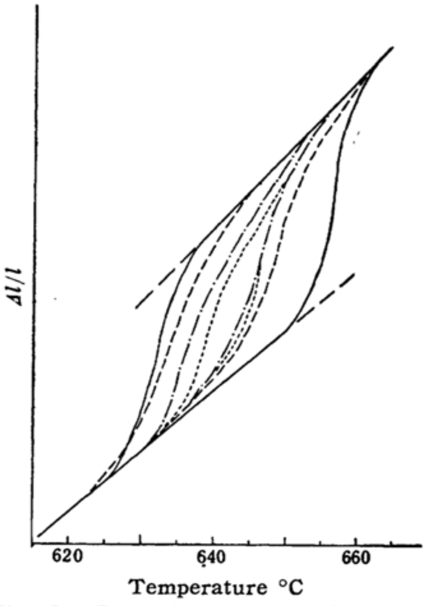

Fig. 3. Expansion curves of ordered specimen around the transition temperature.
——: 100°/hr.; — —: 30°/hr.;
— · —: 5°/hr.; ------: 1°/hr.

745±1° and an anomalous expansion due to the transition is evident.

Detailed measurements were repeatedly made for the ordered specimem at various rates and the resultant hysteresis curves are shown in Fig. 3*. The slower the ascending or the descending rate of temperature, the lower the temperature at which the anomaly takes place. The dilatometric values determined from these curves are as follows;

transition temperature: 745±1°C.,
expansion gap caused by anomaly:
$(32\pm2)10^{-3}\%$,
coefficient before transition:
$(1.20\pm0.03)\times10^{-5}$,
coefficient after transition:
$(1.44\pm0.04)\times10^{-5}$.

Electric Resistance Measurement.— The specific resistance of ordered and disordered pellets of the ferrospinel at the room temperature have the values of 100 MΩ and 2~3 KΩ, respectively. They are more conductive compared with lithium ferrite; especially this phenomenon is remarkable for disordered pellets. The observed d. c. resistance is shown in Fig. 4. In the curve A and B, the value of resistance shows a constant tangent at a lower temperature. Near the transition temperature, resistance decreases anomalously and again shows a linear tangent at a higher region. Although measurements were made not only at different heating rates but also with specimens different in crystal phase, every curve shows a distinct change in conductance at a nearly definite temperature. Compared with the thermal changes, this temperature is concluded to be the transition one. The difference in tangent at the temperature range of the anomaly seems to be related to the different transition velocity corresponding to the heating rate.

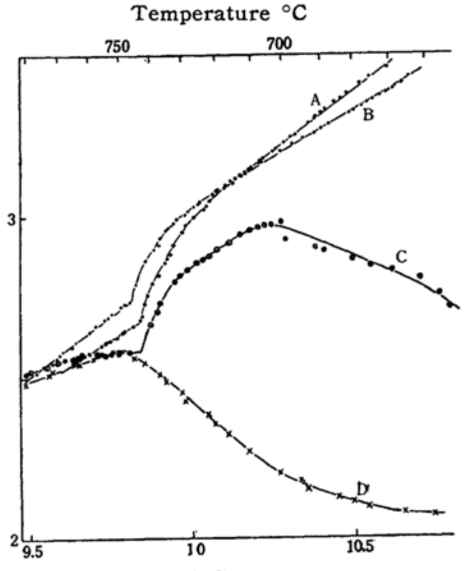

Fig. 4. D. C. resistance curves of $LiFe_5O_8$.
A: ordered specimen; heating rate: 5°/hr.;
B: same as A; heating rate: 30°/hr.;
C: disordered specimen; heating rate: 30°/hr.;
D: same as C; heating rate: 600°/hr.

On the other hand, the curves of a quenched pellet give a negative tangent, which seems to be under the influence of transition to the ordered state of equilibrium from disordered phase at a higher temperature. The temperature range of negative tangent is affected by the heating rate. The values of activation energy are as follows:

0.60 eV: ordered specimen within 200~500°,
0.20 eV: disordered specimen within 130~500°,
1.2~1.4 eV: each specimen after transition.

When the pellets were kept in a stationary d. c. field during the measurements, a color change was observed on the surface as was previously reported for lithium ferrite.

Discussion

It may be convenient to discuss the present results referring to that of lithium ferrite. These compounds take the same kind of transition, i.e. order-disorder transition, but the relative number of the existing two kinds of cation, the same number of lithium and ferric ion, contribute to the transition. For lithium ferrospinel, however, some portions of cations, lithium ions and three times their magnitude of ferric ions at octahedral position, contribute to the transition. Oxygen ions of the ferrite or ferric ions in tetrahedral position and oxygen ions of the ferrospinel, scarcely vary the lattice points by the transition. Regarding only the numbers of migrating ions, the relation between the ferrite and the ferrospinel is analogous to that between β-CuZn and Cu_3Au in binary alloys.

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* As J. B. Austin (*J. Am. Ceram. Soc.*, **35**, 243 (1952).) suggested, the descending curve does not coincide with the ascending one, but it is unavoidable for aggregated specimens used in the present experiments.

Anomalous Expansion.—Anomalous expansions around the transition temperature were observed in the ferrite and the ferrospinel as in the case of other crystals which show the order-disorder transition. The curve of the expansion coefficient of non-stoichiometric compound shows symmetrical form, but that of stoichiometric one shows abrupt λ form. The anomalous gap of expansion was compared with the value calculated from the lattice constant and the numerical results are shown in Table I, where the values obtained by the two methods coincide well.

TABLE I

Compound	% Contraction on Ordering	
	from Lattice Constant	from Expansion Gap
$LiFeO_2$	0.14	0.12
$LiFe_5O_8$	0.036	0.032

Hysteresis and Transition Velocity.—Lithium ferrospinel makes a dilatometric hysteresis curve around the transition temperature, which is shown in Fig. 3. The temperature interval of the hysteresis has about 25° at the rapid rate (100°/hr.). Naturally, the slower the rate, the narrower the interval. The ascending curve at the rate of 1°/hr. is almost the same with that at 5°/hr., but the descending curve of the former is nearer its ascending curve than that of the latter. Under an equilibrated condition, it may be expected that the descending curve will agree with the ascending one and the hysteresis loop vanishes.

Though the transition velocities were not directly measured in the present work, it is of much interest to elaborate the the measurement of the transition velocity with respect to the transition mechanism. The difference in the transition velocities in the ferrite and the ferrospinel can be probably correlated with each crystal structure. This subject should be considered from a crystallographic aspect and also from a diffusion process caused by lattice defect.

Thermal Properties at the Magnetic Curie Point.—There should be a discontinuity in specific heat as ferromagnetic material passes through the Curie point, so that its effect should also appear in the thermal analysis* and dilatometry. As mentioned already, the endothermic reaction around 635° and the increase in expansion coefficient at 590—640° were examined. As for the Curie point, the following data were reported by many authors up to date; 637° (Hilpert et al.[9]), 635° (Kordes and Röttig[4]), 620±2° (Collongues and Chaudron[3]) and 590° (Weisz[7]). From these data, ca. 635° seems to be the ferromagnetic Curie point. Further discussion of the magnetic properties of these materials lies outside of this work.

Transition Temperature and the Composition.—The specimens used in the preceding measurements have the analytical composition $LiFe_{5.86}O_8$. It is necessary to deal with the specimen which has stoichiometric ratio $LiFe_5O_8$, for the purpose of the determination of accurate transition temperature. Several specimens having nearly the stoichiometric composition were prepared and heat-treated under th same condition. The dilatometry was carried out at the rate of 5°/hr. The values of the transition with respect to the composition are shown in Table II.

TABLE II

Composition	Transition Temperature, °C
$LiFe_{4.44}O_8$	749
$LiFe_{4.71}O_8$	751
$LiFe_{4.87}O_8$	749.5
$LiFe_{5.14}O_8$	750
$LiFe_{5.38}O_8$	749
$LiFe_{5.86}O_8$*	745

* The condition of preparation and heat treatment of this specimen is distinguished from others.

In binary alloys, where the homogeneous specimen can be easily prepared, it is well known that the specimen composition affects apparently the transition temperature[10]. On the contrary, in ceramics, it is almost impossible to obtain a homogeneous specimen either in composition or in grain size. This might be the reason why the change in average composition does not affect so appreciably the transition temperature as in the case of alloys. Considering these arguments, the transition temperature of lithium ferrospinel is determined to be 750±1°C.

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* Using differential thermal analysis, Blum et al.. (*Am. Ceram. Sac. Bull.*, **36**, 175 (1957).) detected the Curie point of ferromagnetic and ferroelectric materials.

[9] R. Hilpert, A. Hoffmann and F. Huch, *Ber.*, **72B**, 848 (1939).

[10] F. C. Nix and D. MacNair, *Rev. Sci. Inst.*, **12**, 66 (1941).

Summary

The measurements of differential thermal analysis, thermal expansion and d. c. electric resistance for lithium ferrospinel were performed ; the results were discussed in relation to these for the lithium ferrite. Conclusions are as follows ;

(1) Anomalous changes in the thermal and the electric properties take place during the transition and the hysteresis loops are observed.

(2) The transition temperature for $LiFe_{5.86}O_8$, 745±1°C., is obtained from both thermal and electric measurements. The true transition temperature is determined to be 750±1°C. for the stoichiometric specimen.

(3) It is verified that the transition velocity is more rapid than that of lithium ferrite.

(4) The thermal properties change at the magnetic Curie point, ca. 635°C.

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