Phase Transition of Li_2O-Fe_2O_3 System. III. Long-range Order in Lithium Ferrite and Lithium Ferrospinel

By Eizo KATO*

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In the previous papers[1,2], the thermal and the electric properties of lithium ferrite and lithium ferrospinel were studied from the viewpoint of an order-disorder transition. Then the anomalous phenomena in these properties were observed at the transition.

The order-disorder transition in binary alloys has been widely studied by the statistical thermodynamics[3]. In order to specify the degree of order for the arrangement of atoms, two kinds of order parameters are defined. One is a long-range parameter introduced by Bragg and Williams, and the other is a short-range order parameter introduced by Bethe. When the former parameter is present, some super-stucture reflections appear in an X-ray diffraction. At the transition temperature, this parameter vanishes and the latter parameter remains in a diffuse scattering of X-rays.

The long-range order parameter in a substitutional transition, which was defined by Buerger[4], has not yet been measured except of binary alloys. As the first example of an extension of the transition theory for binary alloys to more complex crystals, temperature dependencies of the long-range order parameter for lithium ferrite and lithium ferrospinel were measured by an X-ray powder method.

Diffraction Theory of Long-range Order

The long-range order parameter S may be written as

$$S=(r_\alpha-p_A)/(1-p_A)=(r_\beta-p_B)/(1-p_B) \quad (1)$$

where r_α is the fraction of α site occupied by A ions and p_A is the fraction of A ions in the crystal, and so forth. S is, of course, defined so that it may be unity for the perfectly ordered state and zero for the perfectly disordered one. When the crystal is of AB type or of AB_3 type, S is given from Eq. 1.

$$S=2r_\alpha-1=2r_\beta-1 \qquad \text{for AB type} \quad (2a)$$

and

$$S=(4r_\alpha-1)/3=4r_\beta-3 \quad \text{for } AB_3 \text{ type} \quad (2b)$$

Let us consider the order-disorder equilibrium, in which two kinds of ions in the crystal contribute to the transition, i.e.,

$$A_aB_bL_l\cdots\cdots N_n \rightleftarrows (A_aB_b)L_l\cdots\cdots N_n$$

where A_a means that a A ions are at the definite equivalent points, and so forth and (A_aB_b) means that a A ions and b B ions are randomly distributed to the points. According to the method used for binary alloys, the expression for the structure amplitude of any state is

$$F=[f_Ar_\alpha+f_B(1-r_\alpha)]G_\alpha + [f_Br_\beta+f_A(1-r_\beta)]G_\beta+\sum_L F_L \quad (3)$$

where f_A is the atomic scattering factor for A ion, f_B that for B ion, G_α and G_β are the geometrical structure factors referring only to the positions of α site and β site respectively, and $\sum_L F_L$ is the sum of structure amplitudes as to L,……, N ions which are independent of the transition. When A_aB_b is AB or AB_3, Eq. 3 is rewritten by introducing Eq. 2,

$$F=S(f_A-f_B)/2\cdot(G_\alpha-G_\beta) + (f_A+f_B)/2\cdot(G_\alpha+G_\beta)+\sum_L F_L \quad \text{for AB} \quad (4a)$$

and

$$F=S(f_A-f_B)/4\cdot(3G_\alpha-G_\beta) + (f_A+3f_B)/4\cdot(G_\alpha+G_\beta)+\sum_L F_L \quad \text{for } AB_3 \quad (4b)$$

For simplicity, both cases are expressed by a single form as

$$F=SF_{ss}+F_{fund} \quad (5)$$

where the subscript *ss* means the superstructure reflection and *fund* the funda-

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* Present address; Idemitsu Kōsan Co., Ltd., Chuō-ku, Tokyo.

[1] E. Kato, This Bulletin, **31**, 108 (1958).

[2] E. Kato, ibid., **31**, 113 (1958).

[3] See, for instances, S. Siegel, "Phase Transformations in Solids", Wiley, New York (1951), p. 366; T. Muto and Y. Takagi, "Solid State Physics", Vol. 1, Academic Press, London (1955), p. 193.

[4] M. J. Buerger, "Phase Transformations in Solids", Wiley, New York (1951), p. 183.

[5] Z. W. Wilchinsky, *J. Appl. Phys.*, **15**, 806 (1944); D. T. Keating and B. E. Warren, ibid., **22**, 286 (1952).

mental reflection. SF_{ss} and F_{fund} correspond respectively to the first term and the rest two terms in Eq. 4.

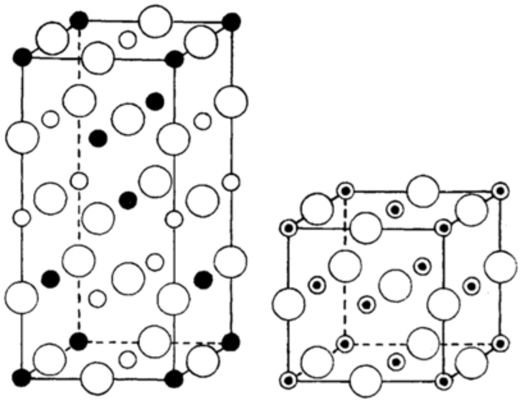
(ordered lattice) (disordered lattice)

Fig. 1. Crystal structures of lithium ferrite.
○ Li^+ ion ● Fe^{3+} ion ○ O^{2-} ion
⊙ $\frac{1}{2}$ $(Li^+ + Fe^{3+})$

The above-mentioned procedures were applied to the transition between $D_{4h}^{19}-I4/amd$ and O_h^5-Fm3m in lithium ferrite, and to that between O^6-P4_33 and O_h^7-Fd3m in lithium ferrospinel. The crystal structures of lithium ferrite are shown in Fig. 1, where oxygen ions are at the same equivalent point in either the perfectly ordered or the perfectly disordered state. The crystal structures of lithium ferrospinel are shown in Fig. 2, where the equivalent points of ferric ions (small shaded circles) at the tetrahedral sites of the eightfold position are the same in either state, and the structural parameter of oxygen ions (large circles) is 0.382[6] at the perfectly ordered state and 0.382± 0.005[7] at the perfectly disordered state. Under the following postulations,

(1) oxygen ions in lithium ferrite, and oxygen ions and tetrahedrally-coordinated ferric ions in lithium ferrospinel are independent of the transition mechanism,

(2) the migrating ions, i.e., all the cations in lithium ferrite or the octahedrally-coordinated cations in lithium ferrospinel, occupy the equivalent points invariable at any state of the transition,

the structure amplitudes of the superstructure reflection can be calculated from Eq. 4 as follows:

For lithium ferrite

$$|F_{ss}|=2\sqrt{2}\,(f_{\mathrm{Fe}}-f_{\mathrm{Li}}),\ h+k=2n+1,$$
$$l=m+1/2\ \ (L=2l=2m+1) \qquad (6a)$$

and for lithium ferrospinel

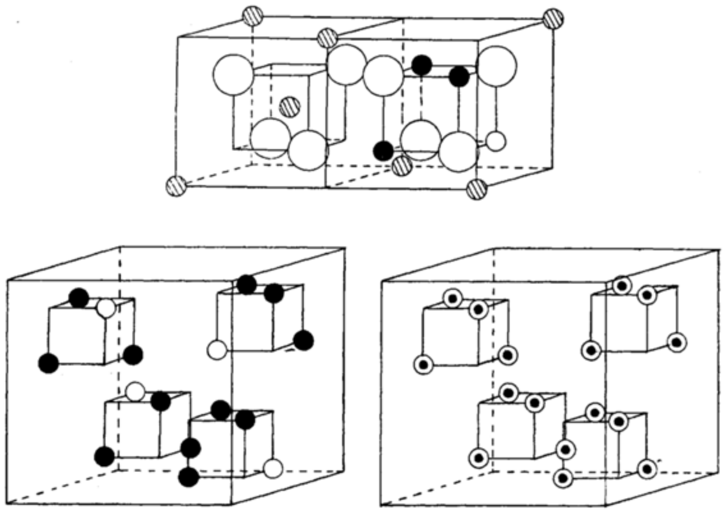
(ordered lattice) (disordered lattice)

Fig. 2. Crystal structures of lithium ferrospinel. Above: One-fourth of a unit cell of the ordered lattice. Below: Total unit cell showing the tetrahedrons of $LiFe_3$.
▨: Fe^{3+} ion at the tetrahedral site ○: Li^+ ion at the octahedral site
●: Fe^{3+} ion at the octahedral site ⊙: $\frac{1}{4}$ $(Li^+ + 3Fe^{3+})$ ○: O^{2-} ion

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[6] P. B. Braun, *Nature*, **170**, 1123 (1952).

[7] F. de Boer, J. H. van Santen and E. J. W. Verwey, *J. Chem. Phys.*, **18**, 1032 (1950).

$$\left.\begin{array}{l} |F_{ss}|=2(f_{Fe}-f_{Li}),\ h,k,l: \\ \qquad \text{one even and two odd} \\ \qquad 2\sqrt{2}\,(f_{Fe}-f_{Li}),\ h,k,l: \\ \qquad \text{one odd, one } 4n, \text{ one } 4m+2 \end{array}\right\} \quad (6b)$$

where f_{Li} is the atomic scattering factor for lithium ion and f_{Fe} that for ferric ion. Here, in lithium ferrite, l indicates the third index of a plane which refers to the cubic unit cell in the perfectly disordered state and L that referred to the tetragonal one in the perfectly ordered state, the latter cell being double of the former along c direction.

Experimental and Results

Specimens.—Lithium ferrite and lithium ferrospinel were prepared by the same method as in the previous papers[1,2]. The probes for X-ray measurements were made by quenching in water after heating for a necessary time at the definite temperatures which were listed in Tables I and II.

TABLE I. ANNEALING TIMES, TEMPERATURE AND VALUES OF S FOR SAMPLES OF LITHIUM FERRITE

Temp. (°C)	Annealing time (days)	Peak area		S
		$A_{10\frac{1}{2}}$	A_{200}	
518	20	4263	2798	0.92
554	21	4928	3017	0.95
587	28	0	—	0
598	28	0	—	0
616	30	0	—	0
627	27	0	—	0
642	15	0	—	0
650	34	0	—	0
661	11	0	—	0

$A_{10\frac{1}{2}}$ in the range of 616∼661°C were measured by the film method.

TABLE II. ANNEALING TIMES, TEMPERATURE AND VALUES OF S FOR SAMPLES OF LITHIUM FERROSPINEL

Temp. (°C)	Annealing time (hr.)	Peak area		S
		A_{210}	A_{220}	
448	53	636	1831	0.95
542	61	688	1839	0.98
652	60	665	1910	0.95
708	64	635	1805	0.96
721	95	623	1816	0.94
744	140	194	1784	0.53
765	24	0	—	0
802	25	0	—	0

Apparatus.—The X-ray reflection intensity was measured by a Norelco diffractometer with filtered Co K_α radiation.

Procedures.—From the observed integrated intensities of a super-structure reflection and a fundamental reflection, S is computed by the following formula,

$$S^2=\left(\frac{P_{ss}}{P_{fund}}\right)\frac{F_{fund}{}^2[m(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{fund}}{F_{ss}{}^2[m(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{ss}}$$

where P: integrated intensity
m: multiplicity
θ: Bragg angle of the reflection

since $F_{ss}=0$ on the fundamental reflection and $F_{fund}=0$ on the super-structure reflection. The integrated intensity is proportional to the area A under the peak curve traced by diffractometer for the reflection, i.e.,

$$P_{ss}/P_{fund}=A_{ss}/A_{fund}$$

Lithium Ferrite.—The super-structure line $10\frac{1}{2}$[8] and the fundamental line 200 were chosen. The final results are listed in Table I.

Lithium Ferrospinel.—The super-structure line 210 and the fundamental line 220 were chosen, and 0.382 was adopted for the value of structural parameter of oxygen ion. The final results are listed in Table II.

Discussion

The statistical theory[9] for the order-disorder transition has been studied on binary alloys. In the simplest case, the approximation is given by Bragg and Williams in which the effect of the nearest neighbors is neglected. Considering the nearest neighbor interaction only, the first approximation is derived from the Bethe's method. Although it may not always be valid to apply the theory for the order-disorder transition in binary alloys to such complex crystals as lithium ferrite and lithium ferrospinel it can be permitted, for the sake of simplicity, to make a trial as follows. Namely, if we neglect the ions which have no direct contribution to the transition, the remaining lattice constructed by the migrating ions alone belongs to the binary system to which the theory may be applied. This lattice is conveniently named a simplified lattice.

The simplified lattice of lithium ferrite belongs to AB type and its disordered lattice is a face-centered cubic. Comparison of the experimental results for lithium ferrite with the curves calculated by the zeroth approximation and the first one for AuCu[10], which is one of binary alloys

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[8] Here is represented the index of the plane referred to the disordered lattice.

[9] See, for instance, E. A. Guggenheim, "Mixtures", Oxford Univ. Press, London (1952), p. 101.

[10] The theory gives the following results: from the zeroth approximation $T/T_c=S/\tanh^{-1}S$, where T_c is the transition temperature; from the first approximation in which all combinations of the quadruplets of sites are considered, the value of S jumps from random value zero to the value $S=0.9828$ at T_c[9].

of face-centered cubic type, is shown in Fig. 3[11]. The experimental results are in qualitative agreement with the curve by the first approximation for AuCu. Comparing the crystal structures of the simplified lattice of lithium ferrite with those of AuCu lattice, both lattices have similar structure in disordered phase. The ordered AuCu lattice is pseudo-cubic (tetragonal but the axial ratio is $1.08:1.08:\sqrt{2}$), while the ordered lattice of lithium ferrite is a tetragonal one which is double the size of cubic lattice in the disordered state along *c* axis as is seen in Fig. 1. However, the number of the nearest neighbor is 12 in either lattice although the relative arrangement of A and B atoms on these 12 positions around the centered atom is different in both lattices. Hence under such a rough assumption as neglecting oxygen ions as mentioned above, lithium ferrite can be approximated to be LiFe as AuCu with respect to its transition.

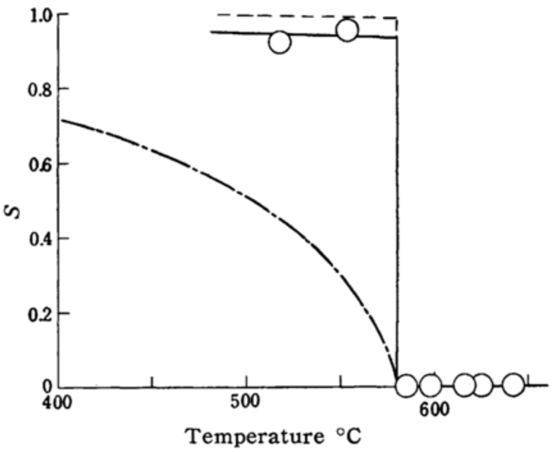

Fig. 3. Variation of long-range parameter for lithium ferrite, experimental and theoretical.
-○-: experimental
- · -: zeroth approximation
------: first approximation

On the other hand, the simplified lattice of lithium ferrospinel belongs to AB_3 type, the typical example of which is $AuCu_3$ (face-centered cubic type). Comparison of the experimental results for lithium ferrospinel with the curves calculated by the zeroth and the first approximation for $AuCu_3$[12] is shown in Fig. 4, where it is found that the experimental results are in good agrreement with the curve calculated by the first approximation. It is noted here that the groups of $AuCu_3$ are arranged side by side along the three directions while those of $LiFe_3$ are arranged tetrahedrally as is seen in Fig. 2, as a result of which the number of the first neighbors is 12 in $AuCu_3$ but 6 in $LiFe_3$[13]. In the present stage the effect of the number of the first neighbor is not ascertained.

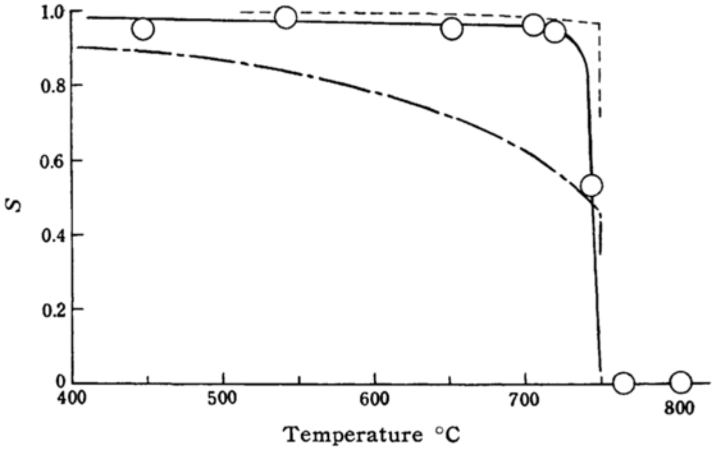

Fig. 4. Variation of long-range order parameter for lithium ferrospinel, experimental and theoretical.
-○-: experimental, - · -: zeroth approximation, ------: first approximation

In conclusion, it is very interesting that

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11) Here T_c is conveniently assumed to be 580°C.

12) The theory gives the following results: from the zeroth aproximation $T/T_c=\frac{4.88\,S}{\ln\{1+16S/3(1-S)^2\}}$; from the first approximation in which all combinations of the quadruplets of sites are considered, the value of S jumps from the random value zero to the value $S=0.9557$ at T_c[9].

13) It may be shown that T_c can not exist in the case of six nearest neighbors (private communication from R. Fujishiro).

in spite of such a rough assumption as ignoring serveral ions having no direct contribution to the transition, statistical theory for order-disorder transition in binary alloys can be approximately applied to estimation of the long-range order parameter in such complex crystals as lithium ferrite and lithium ferrospinel. Moreover, it is emphasized that in the present stage where we have no theory including the effect of all ions in the complex crystal, the assumption of the simplified lattice which can reduce the complex system to a binary one is very useful in treating the order-disorder phenomena.

Transition Temperature of Lithium Ferrite.—As is shown in Fig. 3 the long-range order in lithium ferrite vanishes at 554∼587°C[14]. In the previous paper[1] it was found that the anomalous thermal expansion took place at 660°C in the case of ascending temperature and no change was measured down to 550°C in the case of descending temperature. In both the differential thermal analysis and the electric measurement a change was recognized in the vicinity of 660°C. This discrepancy between the observed transition temperatures by X-ray method and those by others is due to the fact that the samples used in the X-ray method were annealed for a long time (20∼30 days), while the dilatometry was measured under the non-equilibrium condition, because of its sluggish transition.

Transition Temperature of Lithium Ferrospinel.—The value of the transition temperature for lithium ferrospinel was decided to be 750±1°C from the dilatometry. This value was also given from the differential thermal analysis and the measurement of d.c. electric resistance. The diffractometric curves used for the determination of the transition temperature are shown in Fig. 5, where the superstructure lines 210 and 211 are as yet prominent at 744°C, but very faint at 747°C and disappear completely at 756°C. Hence the probable value of the transition temperature can be estimated to be 750°C in good agreement with the value determined by other physical methods.

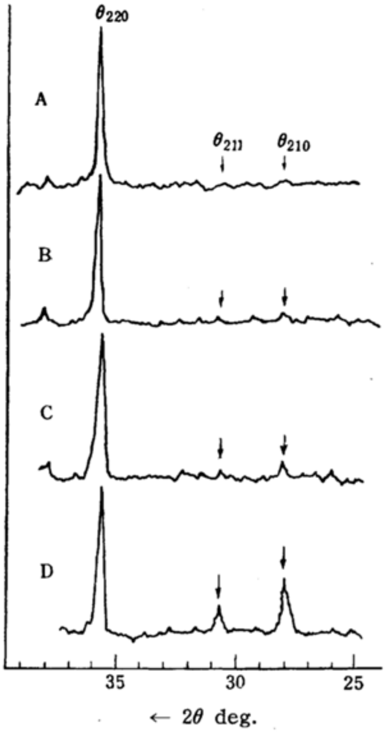

Fig. 5. Diffractometric curves for some samples of lithium ferrospinel in the neighborhood of the transition temperature.
A: 756°C, B: 747°C, C: 744°C, D: 721°C

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Institute of Polytechnics
Osaka City University
Kita-ku, Osaka

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[14] By R. Collongues (*Bull. soc. chim. France*, **1957**, 261) the ordered phase was found at 600°C for a sample annealed for 25 days.