*Phase Transition of Lithium Ferrospinel-Lithium Aluminospinel Solid Solution**

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The phase transition of lithium ferrospinel was studied by means of thermal, electric[1] and X-ray measurements[2]. Lithium aluminospinel is a compound in which ferric ion in LFS changes into aluminum ion. Kordes[3], Verwey[4], Braun[5] and Yamaguchi[6] found that the crystal structure of LAS is the same as that of LFS, but its physico-chemical properties are not evident. No information pertaining to a phase transition of LFS–LAS solid solution has ever been presented in the literature. In the present paper, some physico-chemical changes attributed to exchange ferric ion for aluminum ion in LFS–LAS solid solution are systematically investigated by means of X-ray diffraction and differential thermal analysis, besides, formation of LFS–LAS solid solution is discussed.

Experimental

Specimens*.**—Hydroxides coprecipitated from mixed aqueous solutions of ferric and aluminum nitrate were mixed with lithium oxalate in acetone, then dried, pressed and calcined in an electric furnace at 1200°C for three days. Specimens in a low temperature form (an ordered phase) were obtained by annealing in the same furnace from ca. 1200°C to the room temperature for a day, while specimens in a high temperature form (a disordered phase) were quenched by immersion into water from ca. 1300°C in 1∼2 seconds.

Apparatus and Procedures. — Thermal analyses were carried out up to 1000°C at a heating rate of 10°/min. by the apparatus reported already[7]. The measurements above 1000°C were performed at a rate of 3°/min. by an apparatus with a sample holder of sillimanite. X-ray powder photographs were taken with Co $K\alpha$ radiation by a back-reflection technique, and lattice constants

TABLE I

CHEMICAL COMPOSITIONS, LATTICE CONSTANTS AND ENDOTHERMIC TEMPERATURES OF SOLID SOLUTIONS

Specimen	Composition, Fe/Al	Lattice constant (Å)			Endothermic temperature (°C)
		Ordered phase	Disordered phase	Δ (%)	
A	0/5	7.909	7.911	0.03	ca. 1200
B	1/4	7.999	8.010	0.14	ca. 1130
C	1.5/3.5	8.005 8.206	8.053_6	—	ca. 1090 ca. 880
P	2/3	8.004 8.206	8.095_8	—	875∼880
R	2.5/2.5	8.004 8.206	8.143	—	880
Q	3/2	8.177_3	8.183_8	0.08	916
D	3.5/1.5	8.00 8.210	8.212	0.03	887
E	4/1	8.257	8.263	0.08	826
F*	5/0	8.329_6	8.332_6	0.04	765

* given from the previous report[1]

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* Lithium ferrospinel and lithium aluminospinel are abbreviated to LFS and LAS, respectively, in the following.

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

1) E. Kato, This Bulletin, **31**, 113 (1958).

2) E. Kato, ibid., in press.

3) E. Kordes, *Z. Krist.*, **91**, 193 (1935).

4) E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.*, **15**, 174 (1947).

5) P. B. Braun, *Nature*, **170**, 1123 (1952).

6) G. Yamaguchi, This Bulletin, **26**, 206 (1953).

*** By Kordes[3] lithium fluoride was used as a mineralizer in order to prepare homogeneous specimens. It was proved by X-rays that fluoride was scarcely reacted with ferric oxide, so that this synthesis was not employed.

7) E. Kato, This Bulletin, **31**, 108 (1958).

were accurately determined by an extrapolation method against $1/2(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$

Results and Discussion

Order-Disorder Transition of Solid Solution.—From spacings and reflection intensities measured by X-ray diffraction, the crystal structures of the low temperature and the high temperature form of LFS-LAS solid solution were found to be an ordered lattice, O^6—$P4_33$, and a disordered lattice, O_h^7—$Fd3m$, respectively. Both lattices are identified by arrangements of cations at octahedral interstices, and have the same structures with those in LFS or LAS alone. The values of the lattice constant as a function of the chemical composition for the ordered and the disordered phase of the solid solution are shown in Table I and Fig. 1. The relation of the lattice constants vs. the composition for disordered phases was calculated by a method of least squares.

$$y=7.912_5+0.4907x-0.0699x^2$$

where x is the mole fraction of LFS in the solid solution, and y thelattice constant of disordered phase.

On the other hand, experimental results for the ordered phase were too few to find an equation similar to the above one. Lattice expansions (Δ) at the transition from the ordered phase to the disordered one is small as is listed in Table I, and these values are in 0.03~0.14% regardless of the composition. If the magnitude of the expansion is estimated at 0.05%, the observed values of lattice constant of the ordered phase will agree with those calculated by the above equation.

Physico-chemical changes of the solid solution in occurrence of the transition were observed by differential thermal analysis. The endothermic reaction due to the transition was already seen in the measurement of LFS, and thermal changes similar to LFS or LAS were found in all specimens of ordered phase of the solid solution*. Though the transition temperature of LFS or LAS** is known, no paper was reported for those of the solid solutions. The exact value of the transition temperature had better be measured by a dilatometry with a considerable slower heating rate. The dilatometry was, however, not carried out, because of difficulty to prepare aluminum-rich specimens by sintering. In place of the relation of the transition temperature vs. the chemical composition, that of the endothermic temperature vs. the composition in a series of specimens was measured and is shown

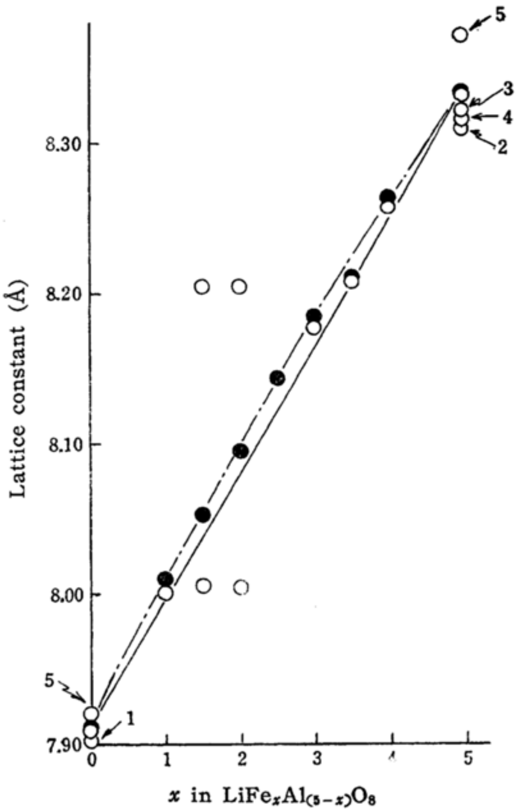

Fig. 1. Relation between the lattice constant and the chemical composition in the solid solutions.
○: ordered phase, present author
●: disordered phase, present author
1: disordered phase, E. Kordes[3]
2: disordered phase, A. Hoffman[9]
3: disordered phase, F. Barblan et al.[10]
4: disordered phase, R. Collongues and G. Chaudron[11]
5: disordered phase, E. Kordes and E. Röttig[12]

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* Thermal analysis of LAS was studied by the present author for the first time. The endothermic reaction due to a ferromagnetism, which was found in LFS, was not observed in the case of the soild solution.

** By Braun[5] the transtion takes place at the temperature below 1350°C.

8) H. Forestier and M. Vetter, *Compt. rend.*, **209**, 164 (1939).

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

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

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

12) E. Kordes and E. Rötting, *Z. anorg. allgem. Chem.*, **264**, 34 (1951).

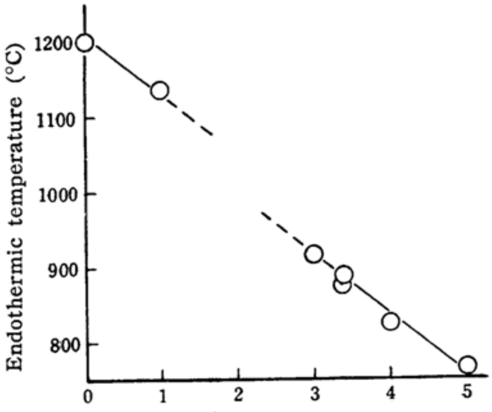

Fig. 2. Relation between the endothermic temperature and the chemical composition in the solid solutions.

in Table I and Fig. 2. The endothermic temperature of LFS is lower than that of any composition of the solid solution, and the more the aluminum content, the higher this temperature. An analogous relation is seen in that of ferromagnetic Curie point vs. chemical composition in nickel-magnesium, cupric-nickel and zinc-nickel ferrospinel solid solution[8]. It is very remarkable that no continuous change of the endothermic temperature against the composition is found in any kinds of specimens of the solid solution but in those of the compositions rich in ferric ion or aluminum ion. This is supposed to be caused by some differences in crystal structure between iron-rich and aluminum-rich compositions. The true transition temperatures, which are provided to be lower than the endothermic temperatures by 10∼30° from the result of LFS, will also be given in the similar manner as above-mentioned.

It is concluded that the transition of LFS–LAS solid solution is the order-disorder transition of the same type as that of LFS or LAS from the results on the crystal structure and the endothermic reaction.

Formation of Homogeneous Solid Solution.—In the disordered phase, homogeneous solid solutions were formed at any compositions. In the ordered phase, however, the solid solutions were homogenized in the specimens of iron-rich composition (D and E in Table I) or of aluminum-rich (B). There might be two phases separated in the specimens of intermediate compositions (C, P and R). The compositions of the separated phases were estimated by the measurements of lattice constants and the use of the above equation, and it was determined that in one of these two phases it is of 20 mole per cent LFS, and in the other 68 mole per cent. In thermal analysis, the only endothermic temperature was measured in the case of specimens B, D and E, while two endothermic temperatures corresponded to two phases were revealed in the case of C, P and R. X-ray diffraction results were in conformity with thermal analysis'. The formation of a homogeneous solid solution in the ordered phase of Q, though it was annealed on the same condition as others, is assumed due to a difference in a disordering velocity* from that of the others. Whether the homogeneous solid solution can be formed in the ordered phase at a higher temperature or in the disordered phase quenched at a lower temperature, no knowledge is offered from the present work.

Homogeneous solid solutions were not formed in the region of 20∼68 mole per cent LFS, where the discrepancy in the relation of the transition temperature vs. the chemical composition was also observed. The conditions necessary to form a homogeneous solid solution are usually those mentioned below[13]; (1) both phases have the same crystal structure, (2) the values of lattice constants resemble each other, (3) the chemical properties are also similar, (4) the ionic radii of constructing ions are the similar size. Typical examples are revealed in the ferrospinel mentioned above, lead phosphate-lead arsenate and lead phosphate-lead vanadate solid solution[14]. Systematic studies on relations of solid solutions of solid solution with order-disorder transition have hitherto been reported very rarely. The ordered phase of LFS and that of LAS have the same crystal structure and the difference between their lattice constants is small. It is also the case in the disordered phase. These is a considerable agreement between an ionic radius of ferric ion (0.67 Å) and that of aluminum ion (0.55 Å). Though having the conditions necessary to be homogenized, LFS–LAS solid solutions cannot

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* From the condition of annealing, the transition velocity of each composition was found to be very rapid as that of LFS.

13) R. Kiriyama and S. Seki, "Crystal Chemistry (Kesshō no Kagaku)", Part II, Sōgensha, Osaka, 1950, p. 135.

14) M. Amadori, *Gazz. chim. Ital.*, **49**, 38 (1919).

be formed over all ratios. Such phenomena might be caused by an averaged structure, i. e., a cation arrangement at the octahedral or the tetrahedral interstices in the crystal. Detailed experiments along this line will be discussed in the following paper.

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