*Cation Arrangement in Lithium Ferrospinel-Lithium Aluminospinel Solid Solution**

By Eizo KATO**

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A cation arrangement in a spinel structure shows how some cations of different valencies are distributed at tetrahedral interstices of the 8-fold position or octahedral ones of the 16-fold position in a spinel lattice, and it has given very interesting subjects concerning a correlation between crystal structure and physico-chemical properties. From the crystallographic aspect a spinel structure is specified into a normal and an inverse type by some difference of the cation arrangement, and only the ferrospinel of inverse structure can reveal ferromagnetism. These fruitful works in solid state physics were presented by Verwey and his co-workers' experiments1) and by Néel's theory2).

Cation arrangement in 2—3 ferrospinel*** solid solution, e.g., nickel-zinc ferrospinel, has been studied not only from the scientific aspect but also in reference to the improvement of magnetic materials3). At present the arrangement of trivalent cations is aimed at which is studied in nickel ferro-aluminospinel4) and other ferro-aluminospinel solid solutions1). In the previous paper5) LFS-LAS solid solution was found to show an order-disorder transition, in addition to showing properties seen in other ferro-aluminospinel solid solutions. On purpose to know correlations between the cation arrangements and other physico-chemical properties, X-ray diffraction intensities were measured and simple magnetic measurements were also carried out.

Experimental

Specimens.—Specimens were synthesized and heat-treated by the method mentioned already5). Specimen codes were A (=LAS), B, C, P, R, Q, D, E and F (=LFS), according to each chemical composition as is shown in Table I. The subscript "L" or "H" was supplied behind the code name of a specimen to show whether it was of ordered or disordered phase.

Apparatus.—X-ray diffraction intensities were measured by Norelco X-ray diffractometer with Co K_α radiation.

Magnitude of magnetization was determined by means of the measurement of distances at which small rods of a sample with dimensions (ca. 0.2 mm. diameter, ca. 3 mm. length) can be attracted by a magnet so as to give a definite attractive force.

Results and Discussion

A general expression of the cation arrangement in LFS-LAS solid solution, $\mathrm{LiFe}_p\mathrm{Al}_{(5-p)}\mathrm{O}_8$, is as follows:

$$[\mathrm{Li}_x\mathrm{Fe}_y\mathrm{Al}_{(2-x-y)}]_{\mathrm{tet}}$$
$$[\mathrm{Li}_{(1-x)}\mathrm{Fe}_{(p-y)}\mathrm{Al}_{(3+x+y-p)}]_{\mathrm{oct}}\mathrm{O}_8$$

where subscript "tet" means the tetrahedral site and "oct" the octahedral site. x and y are the numbers of lithium ions and ferric ions, respectively, located in the tetrahedral site. Then, the average atomic scattering factor for the cation mixture existing in the tetrahedral or the octahedral site, i. e., $\langle f_{\mathrm{tet}}\rangle$ or $\langle f_{\mathrm{oct}}\rangle$, is written as

$$2\langle f_{\mathrm{tet}}\rangle = xf_{\mathrm{Li}} + yf_{\mathrm{Fe}} + (2-x-y)f_{\mathrm{Al}}$$
$$4\langle f_{\mathrm{oct}}\rangle = (1-x)f_{\mathrm{Li}} + (5-y)f_{\mathrm{Fe}} + (3+x+y-p)f_{\mathrm{Al}}$$

where f_{Li} is the atomic scattering factor of lithium ion, f_{Fe} of ferric ion and f_{Al} of aluminum ion.

A cation arrangement in LFS is shown as $[\mathrm{Li}_x\mathrm{Fe}_{(2-x)}]_{\mathrm{tet}}[\mathrm{Li}_{(1-x)}\mathrm{Fe}_{(3+x)}]_{\mathrm{oct}}\mathrm{O}_8$, and $\langle f_{\mathrm{tet}}\rangle$ and $\langle f_{\mathrm{oct}}\rangle$ are written as

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

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

1) For instances, E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.*, **15**, 174 (1947); E. J. W. Verwey, P. W. Haayman and F. C. Romeijn, ibid., **15**, 181 (1947); E. J. W. Verwey, P. B. Braun, E. W. Gorter, F. C. Romeijn and J. H. van Santen, *Z. physik. Chem.*, **198**, 6 (1951).

2) L. Néel, *Ann. phys.*, [12], **3**, 137 (1948).

*** 2—3 spinel means the spinel with di- and tri-valent cations.

3) For instance, R. L. Harvey, I. J. Hegyi and H. W. Leverenz, *RCA Rev.*, **11**, 321 (1950).

4) E. W. Gorter, *Nature*, **173**, 123 (1954); J. S. Smart, *Phys. Rev.*, **94**, 847 (1954).

5) E. Kato, This Bulletin, **32**, 51 (1959).

$$2\langle f_{\text{tet}}\rangle = xf_{\text{Li}} + (2-x)f_{\text{Fe}}$$

$$4\langle f_{\text{oct}}\rangle = (1-x)f_{\text{Li}} + (3+x)f_{\text{Fe}}$$

The same procedure is available in case of LAS. Values of the structure amplitude for reflections were calculated through the above expressions.

Integrated intensity P, which is estimated from structure amplitude F, is proportional to diffractometric peak area A, i. e.,

$$\frac{A_{hkl}}{A_{lmn}} = \frac{P_{hkl}}{P_{lmn}}$$

$$= \frac{[mF^2(1+\cos^2 2\theta)\operatorname{cosec}^2\theta \sec\theta]_{lhk}}{[mF^2(1+\cos^2 2\theta)\operatorname{cosec}^2\theta \sec\theta]_{lmn}}$$

where $h\,k\,l$ and $l\,m\,n$ show Miller's indices for two arbitrary reflections, m=multiplicity and θ=Bragg angle. By measurements of X-ray diffraction intensities for the fundamental reflections, which appear regardless of the existence of a superstructure in the crystal lattice, the cation arrangements can be determined not only in the disordered phase but also in the ordered phase by the above procedures. In order to estimate the cation arrangements in LFS, LAS and LFS-LAS solid solution, reflections 220, 311 and 400 were chosen. The values of the peak area are listed in Table I.

The cation arrangements in LFS and LAS**** are listed in Table II. In this table $[\text{Fe}_{2.0}]_{\text{tet}}[\text{Li}_{1.0}\text{Fe}_{3.0}]_{\text{oct}}\text{O}_8$ was given at both the ordered phase (FL) and the disordered phase (FH) of LFS, which agree with Braun's report6). At the ordered phase of LAS, AL, the cation arrangement is expressed in $[\text{Li}_{0.3}\text{Al}_{1.7}]_{\text{tet}}[\text{Li}_{0.7}\text{Al}_{3.3}]_{\text{oct}}\text{O}_8$ which also agrees with $[\text{Li}_{1/3}\text{Al}_{5/3}]_{\text{tet}}[\text{Li}_{2/3}\text{Al}_{10/3}]_{\text{oct}}\text{O}_8$ given by Verwey3). The error in x measurement decreases with increase in peak area, and the accuracy of x was estimated to range within ±0.05 for LFS and within ±0.1 for LAS.

To determine the cation arrangement in LFS-LAS solid solutions7), it is necessary to assume an adequate value for x, because x and y are variables dependent on each other for any kind of reflection. The following postulations are offered;

1) In LAS a partition of lithium ions to the tetrahedral and to the octahedral site is proportional to that of aluminum ions. In LFS, lithium ions are located only in the octahedral site. In any LFS-LAS solid solution, it is assumed that the partitions of lithium and aluminum ions have the same value regardless of distribution of ferric ions, i. e.,

$$x/(1-x) = (2-x-y)/(3+x+y-p)$$

2) A structural parameter u for oxygen ion has near values both for LFS and for LAS, and u value is almost free in the calculations of structural amplitude in this case. Therefore, u in the solid solutions is assumed to have additive property.

The values of x and y are shown in Table I, and the resultant cation arrangements are listed in Table II. Though numerous errors may be found in the determination of x and y, qualitative conclusions can be proved from experiments of a series of specimens. Lithium ions and ferric ions are located in the different site in the ordered lattice of LFS. In LAS and LFS-LAS solid solution, lithium ions are insufficient in number to be arranged in their proper lattice points (the lithium sites), wherein lithium ions enter for the ordered state of LFS. It is expected that the lithium sites in LAS and LFS-LAS solid solution are occupied by all of the lithium ions in question and the remnants by a few aluminum ions or ferric ions divided into the octahedral site, because the diffraction intensities of LAS and of LFS-LAS solid solution have the same result as that of LFS. Therefore, the crystal structures of low-temperature forms of LAS and of LFS-LAS solid solutions may be considered as those of a sort of disordered state. The lattice points, where aluminum ions are exchanged for ferric ions, are mainly

AL→BL and QL→DL→EL at the tetrahedral site,

BL→CH→PH→RH→QL and EL→FL at the octahedral site.

In the previous paper5), I have reported the distinction in physical properties between LFS-LAS solid solutions of iron-rich composition (above 68 mol. % LFS) and those of an aluminum-rich one (below 20 mol. % LFS). No change takes place in the cation arrangement at the octahedral site in spite of the change from AL to BL. It is considered that this fact makes the aluminum-rich solid solution stable in ordered state. The manner is similar for the cation exchange in the tetrahedral site from EL to FL. It is

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**** As for structural parameter, u, following values were used; LFS: $u=0.382$6); LAS: $u=0.385$1).

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

7) For evaluating x and y, conditions to be satisfied are,

(i) $5\geqq p\geqq 0$ (ii) $p+1\geqq x+y\geqq p-3,\ 2\geqq x+y\geqq 0$

(iii) $1\geqq x\geqq 0$ (iv) $p\geqq y\geqq p-4,\ 2\geqq y\geqq 0$

TABLE I. DIFFRACTOMETRIC PEAK AREAS AND THE VALUES FOR x AND y

Specimen code	Composition, p	Peak area			x	y
		A_{220}	A_{311}	A_{400}		
AL	0	308	831	516	0.2_8	—
BL	1	696	1232	357	0.2_2	0.8_8
CH	1.5	723	1471	473	0.2_7	0.7_8
PH	2	710	1565	485	0.2_8	0.8_8
RH	2.5	865	1791	481	0.2_5	1.0_8
QL	3	815	1673	485	0.3_0	1.1_0
DL	3.5	724	1570	350	0.2_2	1.4_8
DH	3.5	642	1518	450	0.3_3	1.1_5
EL	4	956	2358	434	0.0_8	1.8_2
FL*	5	798	2036	—	-0.0_2	—
FH*	5	767	1902	—	-0.0_6	—

* Peak areas are given from the previous paper[5].

TABLE II. CATION ARRANGEMENT IN LFS-LAS SOLID SOLUTION

Specimen code	Tetrahed. lattice point	Octahed. lattice point
AL	$Li_{0.3}$ $Al_{1.7}$	$Li_{0.7}$ $Al_{3.3}$
BL	$Li_{0.2}$ $Fe_{0.9}$ $Al_{0.9}$	$Li_{0.8}$ $Fe_{0.1}$ $Al_{3.1}$
CH	$Li_{0.3}$ $Fe_{0.8}$ $Al_{0.9}$	$Li_{0.7}$ $Fe_{0.7}$ $Al_{2.6}$
PH	$Li_{0.3}$ $Fe_{0.9}$ $Al_{0.8}$	$Li_{0.7}$ $Fe_{1.1}$ $Al_{2.2}$
RH	$Li_{0.2}$ $Fe_{1.1}$ $Al_{0.7}$	$Li_{0.8}$ $Fe_{1.4}$ $Al_{1.8}$
QL	$Li_{0.3}$ $Fe_{1.1}$ $Al_{0.6}$	$Li_{0.7}$ $Fe_{1.9}$ $Al_{1.4}$
DL	$Li_{0.2}$ $Fe_{1.5}$ $Al_{0.3}$	$Li_{0.8}$ $Fe_{2\ 0}$ $Al_{1.2}$
DH	$Li_{0.3}$ $Fe_{1.2}$ $Al_{0.5}$	$Li_{0.7}$ $Fe_{2.3}$ $Al_{1.0}$
EL	$Li_{0.1}$ $Fe_{1.8}$ $Al_{0.1}$	$Li_{0.9}$ $Fe_{2.2}$ $Al_{0.9}$
FL, FH	$Fe_{2.0}$	$Li_{1.0}$ $Fe_{3.0}$

difficult at present to resolve physical changes in view of the cation arrangement.

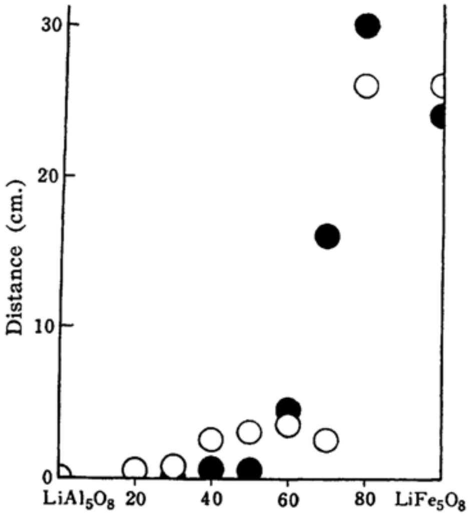

Fig. 1. Magnetization vs. chemical composition.
○: ordered phase
●: disordered phase

Magnetism in a ferrospinel is explained by the theory of ferrimagnetism. Only ferric ions contribute to spontaneous magnetization in LFS-LAS solid solution, and the magnitude of magnetization is related both with the difference between numbers of ferric ions at the tetrahedral and at the octahedral site and with an interaction between cations at the tetrahedral and octahedral site (the latter relating to numbers of ferric ions located in two kinds of lattice point). Fig. 1 shows the relative magnitude of magnetization of LFS-LAS solid solutions at room temperature, measured by the distances capable of attracting specimens by a magnet, as a function of the chemical composition. The observed magnitudes of magnetization qualitatively agree with magnitudes presumed from the cation arrangement.

Now, a quenching effect of LFS-LAS solid solution will be discussed. In specimens C, P and R, magnitudes of magnetization in disordered phase were smaller than those in ordered phase. C, P and R in ordered phase were mixtures of two phases which roughly corresponded to B and D, so that magnetization of specimens was suitable to the resultant magnetization of two phases. When the configurational free energy of crystal lattice is scarcely changed by any cation arrangement, cations, owing to thermal agitation at high temperature, incline to be statistically distributed[8] rather than to be located in the most stable state. In CH, PH, RH, high-temperature form of E and FH, their statistical structures are not recognized. On the other hand, in D, the cation

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[8] "Statistical distribution" means that cations are distributed over all cation sites at random, while "disordered" phase as for ferrospinel indicates a phase in statistical distribution over the octahedral site alone.

arrangement in disordered phase differs from that in ordered phase, and its statistical distribution at a high temperature is recognized from magnetic measurements as well as from X-ray studies. In Q also, the magnetization in ordered phase results in the near magnitude to that in a disordered one, and the statistical distribution is demonstrated. Briefly summarizing, LFS-LAS solid solution gave different cation arrangements within the ordered and the disordered phase in general, but the possibility of the statistical distribution, as is shown in magnesium and cupric ferrospinels, can not yet be determined.

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Institute of Polytechnics
Osaka City University
Kita-ku, Osaka