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Ionic Distribution and Lattice Distorsion of Magnetic Spinels

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§ 1. Introduction

In the crystal lattice of spinels two sites A and B are distinguished for the cation positions, the former is surrounded by oxygen atoms tetrahedrally and the latter octahedrally. The case where the divalent cations are at tetrahedral sites is called normal and the case where the divalent cations are at octahedral sites is called inverse.¹⁾ Beside the above two cases the intermediate type is also found. One can give a parameter x for the proportion of the divalent cations on A sites. It is clear that the normal and inverse spinels are characterized respectively $x = 1$ and $x = 0$.

One of the aims of present study is to criticize the experiments to determine the parameter x for magnetic spinels and to find a rule for the cation distribution.

Besides, it is well known that some magnetic spinels deform their lattices slightly into the ones having lower symmetry in lower temperatures; e. g. magnetite transforms into orthorhombic structure at about 119°K, and hausmannite, copper ferrite, copper chromite etc. transform into tetragonal structure at lower temperature. The second aim of the study is concerned to the above distorsion.

§ 2. Methods to determine the cation distribution

Several methods are applicable to determine the cation distribution, but each method is, by it self, not enough accurate to determine quantitatively the parameter x .

1) Lattice parameter

If the ions are thought to be rigid spheres, the lattice parameters would be different for the normal and the inverse spinels; then we can determine the cation distribution by the measurement of the lattice parameter.

VERWEY²⁾ *et al.* studied the cation distribution by this method. This is convenient, however, the applicability is limited because of the assumption of rigid sphere ions.

2) Magnetic moments

Magnetic spinels are thought to be ferrimagnetic,³⁾ then the total magnetic moment is expressed as difference of the magnetic moments of A and B sublattices. Hence, we can deduce the cation distribution from the measurement of saturation magnetization.^{4,5,6)} Though the accuracy of the magnetic measurement is considerably high, we can hardly decide the distribution, when spinel have several sorts of cations. For spinel other than ferrites, it is likely, that the theory of ferrimagnetism does not always hold.

3) Intensity of X-ray diffraction lines.

BERTAUT^{7,8)} showed a method to determine quantitatively the parameter x by the intensity measurement of X-ray diffraction lines. This is theoretically the most reliable method, however, the measurement of intensity is not so easy, and the experimental accuracy is not always enough high to determine quantitatively the parameter x .

4) Other methods

Beside the above methods, infra-red absorption spectra,^{11,12)} internal friction, electrical conductivity etc. are also related to the cation distribution. But, these are not useful to the aim to determine the parameter x except a few which might be developed in future.

§ 3. Theories for the cation distribution

The cation distribution of a spinel is theoretically decided to minimize its free energy $F=U-TS$, where U means the internal energy, which consists of MADELUNG's energy, repulsive energy and the electronic energy.

Magnetic ferrites are thought to be ionic crystals, then it is naturally to assume MADELUNG's energy V is the most important. For a spinel lattice V is given by

$$V = -\frac{1}{2} \frac{e^2}{a} (pM_A + 2qM_B + 8M_O) = -M \frac{e^2}{a}$$

where M_A , M_B and M_O means respectively MADELUNG's constants of A, B and oxygen sublattices, and p and q mean the average charges of A and B sites respectively.

VERWEY *et al.*^{13,14)} calculated MADELUNG's constants M of normal

and inverse 2-3 and 4-2 spinels as functions of the oxygen parameter u , which indicate the position of oxygen ions. (Fig. 1). VERWEY tried to

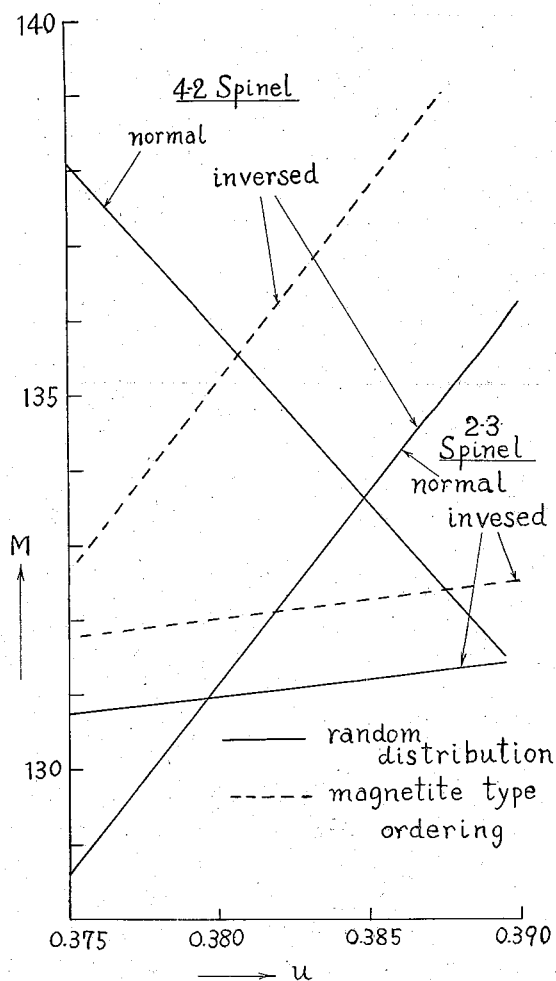


Fig. 1.

energy in crystal differs from those of free ions. The crystalline field having cubic symmetry removes degeneracy of d -level into two levels. DUNITZ, ORGEL¹⁵⁾ and MCCLURE¹⁶⁾ studied the separation of the levels by spectroscopic data and calculated the B site preference energy, i.e. the difference of electronic energies of A site and B site, of various ions in magnetic compounds, which is tabulated in Tab. 1.

explain the cation distribution by MADELUNG's energy. However, some spinels fail to be explained; e.g. CuFe_2O_4 and ZnFe_2O_4 have equal u value ($u=0.380$), nevertheless, the former is inverse and the latter is normal.

At the calculation of MADELUNG's energy the ions are assumed as electric point charges. Actually, however, the ions have repulsive force. It is difficult to take the repulsive force exactly into account, we make the following neglect. Since repulsive potential vanishes rapidly against the ionic distances, we assume the ions as a rigid sphere, whose parameters are decided empirically and take only electrostatic energy.

By electronic energy one means the energy of electron cloud of individual ion. Naturally electronic

TABLE 1.

	A	B	C	D	E
Mn ²⁺			0	0	0
Fe ²⁺	10400	10400	11.9	7.9	4.0
Co ²⁺	9700	9700	22.2	14.8	7.4
Ni ²⁺	8500	8500	29.2	8.6	20.6
Cu ²⁺	12600	12600	21.6	6.4	15.2
Ti ³⁺	20300	18300	20.9	14.0	6.9
V ³⁺	18600	16700	38.3	25.5	12.8
Cr ³⁺	17400	15700	53.7	16.0	37.7
Mn ³⁺	21000	18900	32.4	9.6	22.8
Fe ³⁺			0	0	0

A: (cm⁻¹) in hydrates.B: (cm⁻¹) in oxides.

C: octahedral stabilization (Kcal/mole).

D: tetrahedral stabilization (Kcal/mole).

E: excess octahedral stabilization (Kcal/mole).

They attempted to explain the cation distribution from the electronic energy, and their attempts seem to be successful (see Tab. 2), but the following questions still remain.

- 1) Why Mg ferrite is inverse and Mn, Zn, Cd ferrites are normal?
- 2) Why NiAl₂O₄ is inverse and other aluminates are normal?

TABLE 2.

	Fe ³⁺		Cr ³⁺		Mn ³⁺		Al ³⁺	
		x		x		x		x
Mg ²⁺	0	*0.1 ⁽¹⁾ *0.12 ⁽²⁾	N(37.7)	1 ⁽¹²⁾	N(22.8)	1 ⁽¹²⁾	0	1 ⁽⁹⁾
Mn ²⁺	0	*0.8 ⁽³⁾	N(37.7)	1 ⁽⁹⁾	N(22.8)		0	0.66 ⁽¹⁴⁾
Fe ²⁺	I (4.0)	* 0 ⁽⁴⁾	N(33.7)	1 ⁽⁹⁾	N(18.8)		I (4.0)	1 ⁽⁹⁾
Co ²⁺	I (7.4)	* 0 ⁽⁵⁾	N(30.3)	1 ⁽⁹⁾	N(15.4)		I (7.4)	0.81 ⁽¹⁴⁾
Ni ²⁺	I (20.6)	* 0 ⁽⁶⁾ (16)	N(17.1)	1 ⁽¹¹⁾ (9)	N (2.2)	0 ⁽¹³⁾ (17)	I (20.6)	0.15 ⁽¹⁴⁾
Cu ²⁺	I (15.2)	* ⁽⁷⁾ 0.05 ⁽⁸⁾	N(22.5)	*1 ⁽⁸⁾ ⁽¹⁰⁾ 0.9 ⁽⁸⁾	N (7.6)	1 ⁽¹²⁾	I (15.2)	0.66 ⁽¹⁵⁾
Zn ²⁺	0	*0.95 ⁽⁶⁾	N(37.7)	1 ⁽¹⁾	N(22.8)	1 ⁽¹³⁾	0	1 ⁽⁹⁾
Cd ²⁺	0	1 ⁽¹²⁾	N(37.7)	1	N(22.8)	1	0	1

* neutron

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§ 4. A theoretical consideration for the cation distribution

To explain the cation distribution completely, one should calculate simultaneously the lattice structure itself, esp. oxygen parameter. We might calculate the oxygen parameter by the rigid sphere assumption. In fact, however, we do not know the exact information about ionic radii in spinels.

If oxygen ions construct close-packed structure, the parameter u is equal to 0.375. Cations on A site or B site change the position of oxygen by δ , then δ be expressed approximately lineally to r_A as

$$\delta = ar_A + b(r_B, r_O).$$

At the normal 2-3 spinel, r_A is the radius of divalent ion and r_B and r_O are radii of trivalent ions and oxygen respectively. The constants a and b are chosen in the following way. In MgFe_2O_4 and ZnFe_2O_4 , electronically, Mg and Zn are equally favorable to A or B sites, because both ions are in singlet state. Then, the ionic distribution would be determined by MADELUNG's energy. If we suppose that inverse spinel has, at least, short range order, then from the calculation by VERWEY, the normal

structure is stable for $u > 0.81$, and inverse is stable for $u < 0.81$. The fact, that MgFe_2O_4 is inverse and ZnFe_2O_4 is normal, leads to the conclusion that $u = 0.81$ corresponds to the atomic radius between Zn^{2+} and Mg^{2+} . The other fact to decide the constants is distortion of CdAl_2O_4 . Cd is the largest ion observed in stable spinel structure. The largest deformation allowable for a stable spinel is geometrically given: $\delta = 0.0125$. From these two facts the relation between δ and r_A is given, which is shown in Fig. 2. Observed oxygen parameters u agree satisfactorily with the above relation. By using this relation we can easily obtain MADELUNG's energy by mean of VERWEY's Figure.

If we take both MADELUNG's energy and electronic energy simultaneously, the cation distribution is quite well explained. For instance NiMn_2O_4 must be normal by electronic energy only (2.2 Kcal/mol), however, if one take MADELUNG's energy together into account, normal structure would lose 120 Kcal/mol, and NiMn_2O_4 must be inverse. Another example is NiAl_2O_4 . It gains 19.2

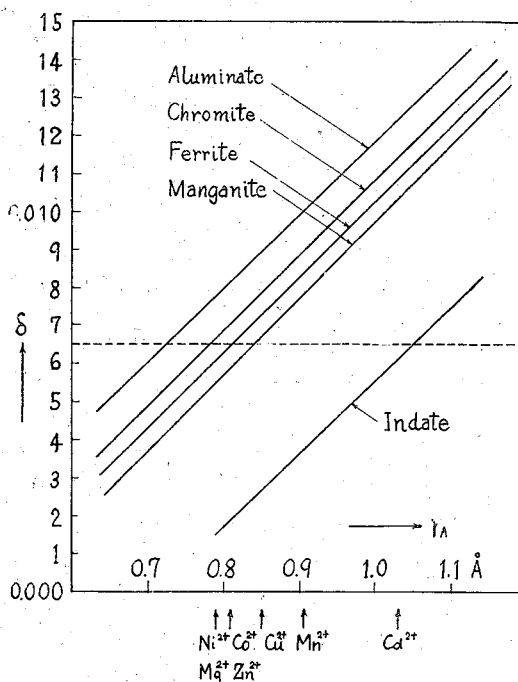


Fig. 2.

Kcal/mol in MADELUNG's energy for normal structure, however, it loses 20.6 Kcal/mol electronically, and NiAl_2O_4 must be inverse. On the other hand CuAl_2O_4 gains more energy electrostatically than the electronic energy lost in normal structure, and the compound is normal.

Thus, the cation distribution of all spinels hitherto studied are explained without exception.

§ 5. Distorsion of crystal lattice of spinels

Various spinels exhibit tetragonal distortion, and its origin was discussed

by several authors.* GOODENOUGH¹⁷⁾ explained the distorsion of spinels by covalent bond between ions. For instance, in CuFe_2O_4 valence electrons of copper make (dsp^2) orbital of square type, and it causes c/a to increase. This explanation, however, is not appropriate for CuCr_2O_4 , since where c/a decreases.** DUNITZ and ORGEL¹⁸⁾ explained the distorsion by the JAHN-TELLER effect, i.e. lowering electronic energy by deformation to lower crystal symmetry.

Crystal distorsion of the following compounds were experimentally studied. We exclude magnetite, because it is believed that its distorsion is caused from different origin. (Low temperature transformation of magnetite, cubic $\rightleftharpoons$ orthorhombic, is considered as order-disorder transformation of Fe^{++} and Fe^{+++} ions on B sites.)

1) Spinel including Cu^{++} ion

Cu^{++} is a ion responsible to crystal distorsion, and various compounds are studied. Mixed spinel of CuFe_2O_4 and CuCr_2O_4 are studied by MIYAHARA, OHNISHI¹⁹⁾ and TERANISHI. DELORME¹⁹⁾ studied $\text{GeCo}_{2-t}\text{Cu}_t\text{O}_4$, $\text{Cu}_{1-t}\text{Me}_t\text{Fe}_2\text{O}_4$ and $\text{Cu}_{1-t}\text{Me}_t\text{Cr}_2\text{O}_4$ ($\text{Me}=\text{Ni}, \text{Co}, \text{Mg}, \text{Zn}, \text{Cd}$). In CuFe_2O_4 - CuCr_2O_4 series Fe-side deforms to tetragonal structure: $c/a > 1$, while Cr-side: $c/a < 1$. In $\text{GeCo}_{2-t}\text{Cu}_t\text{O}_4$ series tetragonal distorsion is observed in the region $0.25 < t < 0.6$, whose maximum axial ratio is 1.034.

2) Spinel including Mn^{+++} ion

Hausmannite and zinc manganite are studied by MASON^(3,9) and found, that it deforms tetragonally below 1170°C and 1025°C resp. Recently SINHA^(3,9) *et al.* studied various manganites and lattice parameters were measured. Manganites except NiMn_2O_4 and CuMn_2O_4 exhibit tetragonal distorsion. FINCH²⁰⁾ *et al.* studied the manganite-ferrite system ($\text{Me}=\text{Ni}, \text{Mn}, \text{Co}, \text{Fe}$). MURAMORI^(2,12) studied Cu and Mg ferrite-manganite system. From the above experiments it is commonly concluded that the tetragonal distorsion takes place when content of Mn ions exceeds 50%, and volume change is hardly observed between cubic and tetragonal phases.

3) Other spinels.

FRANCOMBE^(3,6) studied $\text{Fe}^{++}\text{Fe}_{2-t}^{+++}\text{Cr}_t\text{O}_4$ system and found that the

* Note added in proof: The author has an opportunity to read the Thesis (Grenoble 1956) by C. DELORME, who studied lattice distorsion of various mixed spinels including Cu^{++} ion. He stated that deformation is caused by Cu^{++} , Ni^{++} and Mn^{+++} ions and their neighbors.

** Goodenough insists that his theory also holds for this case.

crystal at low temperatures is cubic for $t < 1.0$, tetragonal for $1.0 < t < 1.4$ and orthorhombic for $1.4 < t < 2.0$. MCGUIRE⁽²¹⁾ et al. studied $\text{NiFe}_{2-t}\text{Cr}_t\text{O}_4$ systems and found that the crystal is tetragonal ($c/a < 1$) for $1.25 < t < 1.75$, orthorhombic for $1.75 < t < 1.85$ and tetragonal ($c/a > 1$) for $t > 1.85$. ROOKSBY^(3,1) et al. found tetragonality $c/a = 0.9988$ in cobalt ferrite at the liquid nitrogen temperature.

These results are shown in Tab. 3.

TABLE 3.

	Fe^{3+}		Cr^{3+}		Mn^{3+}		Al^{3+}	
	theor	exp.	theor	exp.	theor	exp.	theor	exp.
Mg^{2+}	0	cubic	0	cubic	$c/a > 1$	$c/a = 1.15^{(8)}$	0	cubic
Mn^{2+}	0	"	0	"	$c/a > 1$	$c/a = 1.16^{(9)}$ 1170°C ⁽⁹⁾	0	"
Fe^{2+}	weak	orth. -160°C ⁽⁵⁾	weak	$c/a = 0.968^{(6)}$ -90°C	$c/a > 1$	$c/a = 1.05$	weak	"
Co^{2+}	"	$c/a = 0.9988^{(1)}$	0	cubic	$c/a > 1$	$c/a = 1.12$	0	"
Ni^{2+}	0	cubic	$c/a > 1$	$c/a = 1.025^{(7)}$ 36°C ⁽⁷⁾	$c/a > 1$	cubic	0	"
Cu^{2+}	$c/a > 1$	$c/a = 1.056^{(2)}$ 360°C ⁽³⁾	$c/a < 1$	$c/a = 0.913^{(2)}$ 610°C ⁽⁴⁾	$c/a > 1$	"	$c/a > 1$	"
Zn^{2+}	0	cubic	0	cubic	$c/a > 1$	$c/a = 1.14^{(9)}$ 1025°C ⁽⁹⁾	0	"
Cd^{2+}	0	"	0	"	$c/a > 1$	$c/a = 1.20^{(8)}$	0	"

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Tetragonal distortion of these compounds are explained by the JAHN-TELLER effect as mentioned above. But some spinels should be explained in connexion with cation distribution. In the followings some problems of special interests are discussed.

1) NiMn_2O_4 and CuMn_2O_4

The reason that the above two manganites are cubic, is explained as

follows: NiMn_2O_4 is known as an inverse spinel and B sites include only a half of manganese ions. As study of mixed manganites suggests, distorsion is caused when the content of Mn ions in B sites exceeds 50%. Hence, inverse nickel manganite remain cubic. In CuMn_2O_4 copper ion in B sites which would cause $c/a > 1$ and manganese ion in A site which would cause $c/a < 1$ compensate each other and no distorsion take place.

2) CuAl_2O_4 and FeAl_2O_4

The above compound, of which one expects some distorsion, have not been studied in detail. It is reported that CuAl_2O_4 does not exhibit any distorsion at ordinary temperature. In this case Cu ions on A-sites which would cause an opposite distorsion compensate the effect of Cu ions on B-sites.

3) Tetragonality and transformation temperature

It is noteworthy that all spinels which deforms tetragonally at lower temperature exhibit a relation between tetragonality $\sigma = |c-a|/a$ (at low temperature) and the transformation temperature T_c . The relation is

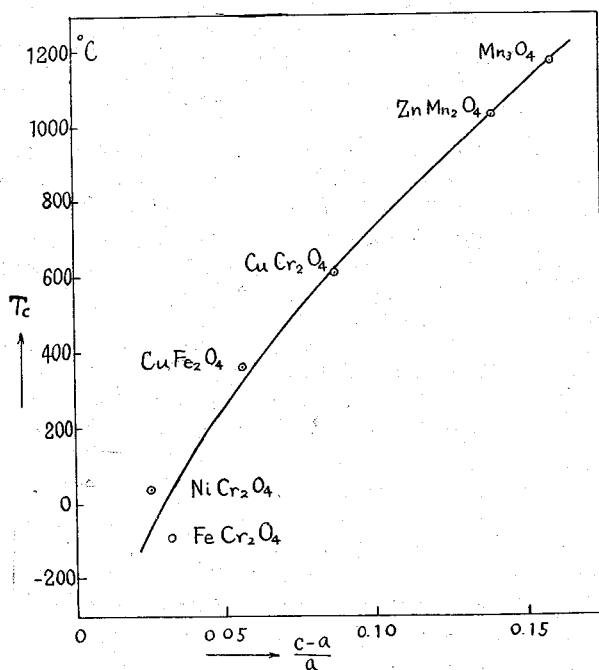


Fig. 3.

expressed in a curve for ferrites, chromites, manganites and aluminates (Fig. 3). This fact suggests that deformation of magnetic spinels is caused from the same origin, i.e. the JAHN-TELLER effect.

4) From the above discussed facts we have some questions about FRANCOMBE's analysis(3.6) for the crystal structure of $\text{FeFe}_{2-t}\text{CrO}_4$ system, where the compounds of $t > 1.0$ are thought to be normal, hence it is not naturally to think $(c-a)/a$ reverse its sign in the normal region. On the other hand we know that in some copper ferrite-chromites cubic and tetragonal phases co-exist. If we re-analyze FRANCOMBE's data, so-called

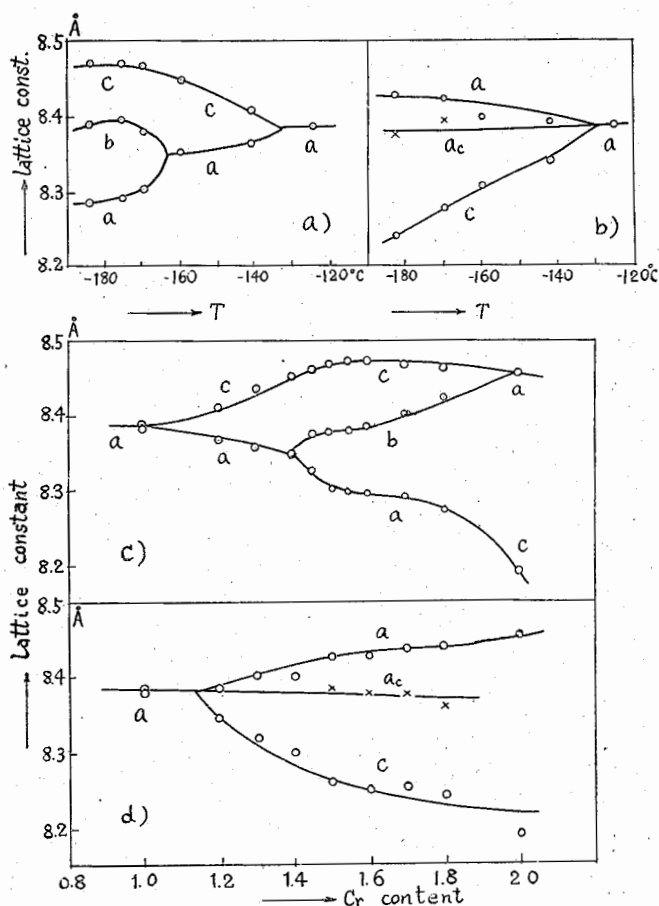


Fig. 4.

orthorhombic phase is explained as cubic and tetragonal phases in co-existence. FRANCOMBE's analysis is shown in Fig. 4 a, c and the re-analyzed results in Fig. 4 b, d.

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