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Systematics of the Lattice Constants in the Homologous Compounds, (RMO_3) $(M'O)_m$, by the "Extended Vegard's Law"

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Lattice constants of the homologous compounds, (RMO_3) $(M'O)_m$ [R: Sc, In, Y, or rare-earth element between Ho and Lu; M: Fe, Ga or Al; M': Mg, Mn, Fe, Co, Cu, or Zn] are analyzed on an assumption that the coordination polyhedra of all cations couple elastically to make up the periodic lattice of the crystal at the lowest energy state. This is a natural extension of Vegard's law, which can be considered as an extreme case of the present model where the "elastic" constant of the coordination polyhedra is identical, irrespective of the cation. A wide range of compounds is covered by the analysis. "Elastic" constants and the proper dimension of each coordination polyhedron are estimated. An anomaly disclosed on RFe_2O_4 is attributed to the charge fluctuation between Fe^{2+} and Fe^{3+}.

1. Introduction

Quantitative explanation of the dependence of the lattice dimensions on the constituent elements is one of the important aims of crystal chemistry. In the present paper, we show that the lattice constants of almost all the compounds belonging to a family of oxides, (RMO) $(M'O)_m$, can be analyzed successfully by a simple model. By the model, coordination polyhedra of all the cations are assumed to couple elastically and the state of the lowest "elastic" energy is realized. Parameters to be determined are the "proper" dimensions and the "elastic constants" of polyhedra. The former is the dimensions of the polyhedron in a hypothetical crystal which is composed of that coordination polyhedron only, and the latter is the coefficient of the energy increase proportional to the square of the deformation of the polyhedron from the "proper" value.

A family of oxides $(RMO_3)_n$ $(M'O)_m$ crystallizes in a hexagonal layered structure (*1*). Here, R stands for Sc, In, Y, or a rare-earth element from Ho to Lu, and M, and M' stand for 3+ Al, Fe, or Ga, and Mg or 2+ transition-metal ions from Mn to Zn except

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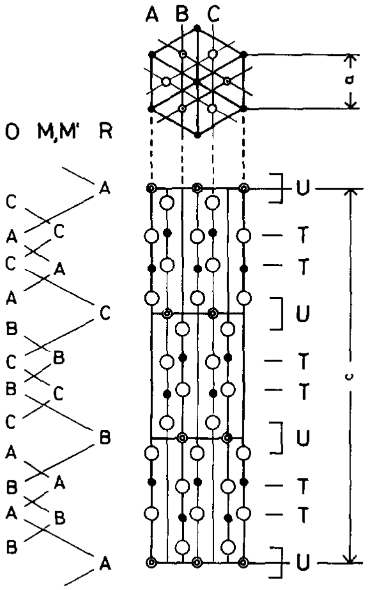


FIG. 1. Crystal structure of $RMM'O_4$. Double circles are for R, solid circles are for M or M', and open circles are for O.

Ni, respectively, where m or n is an integer. The crystal structure of the end member of this series for $n \rightarrow \infty$ is the hexagonal $YAlO_3$ type, that was reported by Bertaut and Mareschal in 1963 (*2*). The structure of the other end member for $m \rightarrow \infty$ is wūrtzite type. In the following, the notation of (n, m) compound is used. The crystal structure of the (1, 1) compound, center of this series, is shown in Fig. 1, as an example. In this structure, each element, R, M and M' or O, makes up planar triangular nets in the c plane and the nets stack along the c axis. No evidence has been found so far for any preferential location of M and M', except the isolated layer of M + O (named T in the figure) which appears in the case of $n > 1$ (see Fig. 2).

By stacking triangular lattices, three kinds of lattices can be distinguished according to the position of atoms. These three will be assigned as A, B, and C, as usual (see the upper part of Fig. 1). The crystal structure of all the members of this series of compounds can be constructed by the following terms:

1° R is coordinated by six oxygen ions octahedrally. Thus, the stacking is, for example, C(O)–A(R)–B(O). This block of three layers of atoms is denoted U in the figure.

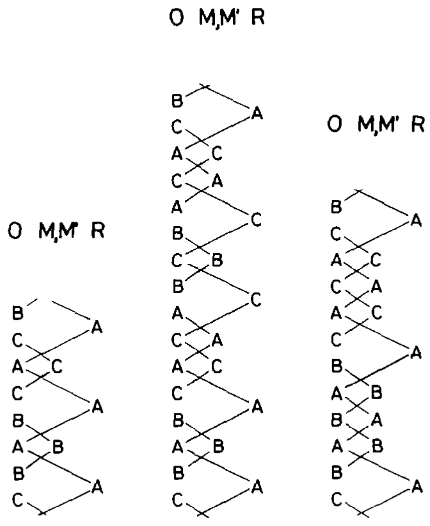
2° A layer of M and M' and that of oxygen lie in nearly the same plane. These layers, B(M, M')–A(O), for example, are a characteristic of this family and are named T.

3° U and T stack along the c axis to make the anion and cation net nearest, i.e., A(R)–A(O), B(O)–B(M, M'), etc. The oxygen layer A in the former example is of the T layer next to the U block, and that B in the latter is of the U block or of the neighboring T. (See the left-hand side of Fig. 1.) This condition is easily understood as due to the interlayer Coulomb energy.

By the two conditions above, M and M' ions are coordinated by five O^{2-} ions forming a trigonal bipyramid.

Some examples of the crystal thus constructed are shown in Fig. 2. The symmetry of the crystal is $P6_3/mmc$ when $n + m$ is odd and $R\bar{3}m$ when $n + m$ is even. In the latter case, the crystal is rhombohedral but, for convenience, the hexagonal frame is used in this paper. Note that the dimension of the triangular net, A, B, or C, is just the lattice constant a of the crystal.

Such a simple way of crystallization being considered, it is not surprising that the lattice constants, a and c, change systematically according to the constituent elements. In the case of RFe_2O_4, for example, the crystal shrinks along the a axis almost linearly with increasing atomic number of R, from Ho to Lu, whereas c increases. (See Figs. 3 and 7 below.) Qualitatively, this has been considered to be due to the change of the ionic radii of rare-earth ions: the size of the coordination octahedron of R in the U block is larger along the a axis when the ionic radius of R^{3+} is large. In reality, however,



(1,0) (2,1) (1,2)

FIG. 2. Stacking of the triangular nets of R, (M, M'), and O along the c axis in the homologous compounds $(RMO_3)_n(M'O)_m$.

M and M' also affect the lattice constants. It can be considered that the oxygen nets, octahedra in U and triangles in T, have their proper dimension according to the cations at the center and interact to make up the whole crystal at the lowest energy state.

The purpose of this paper is to show that the lattice constant a of this series of compounds can be analyzed (semi-)quantitatively by an elastic model:

(i) Each U block (RO_2) and T layer ($(M, M')O$) is assumed "elastic," i.e., energy of them is proportional to the square of their deformation from the proper dimension.

(ii) The lattice constant a is determined to make the total "elastic" energy of the lattice minimum.

This is a natural extension of the Vegard's law, where the elastic constant of each coordination polyhedron is assumed identical for all the atoms and only the proper dimension of each polyhedron is considered different: lattice constants of the mixed crystal are given by the weighted mean of the dimension of the coordination polyhedra of constituent elements.

In the present treatment, there are two parameters, proper dimension and "elastic" constant, for each coordination polyhedron of cations, R, M or M'. Taking into account the above-mentioned dependence of the lattice constant on the atomic number of R, we add an assumption, to minimize the number of parameters. That is:

(iii) The rigid-sphere approximation can be adopted to the coordination octahedron of the rare-earth element, R, and the "elastic" constant can be assumed identical for all R. Validity of the rigid-sphere approximation is discussed in Section 4. This assumption (iii) is not sufficient to determine $a(R)$, the proper dimension of the coordination octahedron of R. We add the following assumption:

(iv) In the free U block, oxygen ions in the upper and the lower layers contact with each other.

Though not for all of the compounds, the "elastic" or extended Vegard's model was found valid for a wide range of compounds and the proper dimension of the coordination triangle of each set of transition elements, $a(M, M')$, and the "elastic" constant, $K(M, M')$, were determined. On the above assumptions, analysis can be extended to $a(M, M')$ and $K(M, M')$ to express them as linear combinations of a and K of each transition element, respectively. Then, we can compare the data of the compounds with different m or n. It was disclosed that the proper dimension of the oxygen triangle coordinating Zn coincides with the lattice constant a of wurtzite.

Another lattice constant, c, is considered subsequently. The dimension of the U block along the c axis, c(U), can be estimated by assumption (iii) and the experimentally determined a. Then, the dimension along the c axis of the double T layers in the (1, 1) compound, for example, can be deduced from the observed lattice constant c (See Fig. 1). One-third of this quantity is the average distance between the oxygen nets out of a U block and is denoted as $c(\mathrm{T})$. It is disclosed that almost all $c(\mathrm{T})$ of (1, 1) compounds is expressed by a universal linear function of $a/a(M, M')$, provided that $c(\mathrm{T})$ are normalized by a factor dependent on M and M'. In the case of $M' = \mathrm{Zn}$, only for which compounds with $m > 1$ have been synthesized systematically, $c(\mathrm{T})$ increases with increasing m and tends to 2.603 Å for $m \rightarrow \infty$, just one-half of the lattice constant c of wūrtzite.

In the following, the lattice constants of the (1, m) compounds at room temperature, accumulated in Table 26 of Ref. (*1*), are used. The analysis of a is carried out and the parameters are determined in the next section. The relation between the lattice constants c and a is considered in Section 3 and the results are discussed and assumptions and procedures reexamined in Section 4. Compounds of $n > 1$ will not be treated since the available experimental data are not enough at present.

2. Analysis of *a*

The basis of the present analysis is the following equation:

$$E = n\{K(R)(a(R) - a)^2 + K(M)(a(M) - a)^2\} + mK(M')(a(M') - a)^2. \quad (1)$$

Here, E is the energy of the compound $(RMO)_n(M'O)_m$, a is the lattice constant of the crystal along the a axis, $a(R)$ and $K(R)$, etc., are the proper dimension and the "elastic" constant, respectively, of the coordination polyhedron of R, etc. By the minimization of this energy, a is given as

$$a = \frac{n(K(R)a(R) + K(M)a(M)) + mK(M')a(M')}{n(K(R) + K(M)) + mK(M')}. \quad (2)$$

According to assumption (iii) in the last section, the atomic distance of R and the coordinating O, $r(R\text{–O})$, is equal to the sum of the ionic radii of R^{3+} and O^{2-}:

$$r(R\text{–O}) = \sqrt{a^2/3 + c(\mathrm{U})^2/4} = r(R) + r(\mathrm{O}). \quad (3)$$

Here, $c(\mathrm{U})$ is the dimension of the U block along the c axis and $r(R)$ and $r(\mathrm{O})$ are the ionic radii of R^{3+} and O^{2-}, respectively. In the following, we use the value given by Shannon and Prewitt (*3*) for rare earths, based on the oxygen radius of 1.40 Å; $r(\mathrm{In}^{3+})$ was assumed to be 0.792 Å. As for the Sc-compounds, experimentally determined lattice constants correspond to $r = 0.76$–0.77 Å, much larger value than the Shannon–Prewitt radius (0.73 Å).

To determine $a(R)$, assumption (iv) is necessary. That is,

$$r(\mathrm{O\text{–}O};\mathrm{U}) = \sqrt{a(R)^2/3 + c(\mathrm{U})^2} = 2\,r(\mathrm{O}). \quad (4)$$

Then, $a(R)$ is given from Eqs. (3) and (4) as

$$a(R) = 2\sqrt{r(R)\,(r(R) + 2r(\mathrm{O}))}. \quad (5)$$

The values of $a(R)$ are tabulated for In, Lu, Yb, Tm, Er, Y, and Ho in Table I with their ionic radii.

The lattice constants of many (1, 1) compounds with different R, M, and M' have been reported and were tabulated in Ref. (*1*, Table 26). a of the compounds with the same M and M' increases almost linearly with increasing ionic radius of R. According to Eq. (2), they can be expressed as

$$a = \frac{K(R)a(R) + K(M, M')a(M, M')}{K(R) + K(M, M')}. \quad (6)$$

TABLE I

THE LATTICE CONSTANT a OF THE FREE U BLOCK ESTIMATED ON THE RIGID-SPHERE APPROXIMATION, $a(R)$, AND THE IONIC RADII[a] $r(R)$, OF RARE-EARTH ELEMENTS AND In (Å)

R	In	Lu	Yb	Tm	Er	Y	Ho
$r(R)$	0.792	0.848	0.858	0.869	0.881	0.892	0.894
$a(R)$	3.373	3.518	3.543	3.571	3.602	3.630	3.635

[a] These are the values given by Shannon and Prewitt (3) on the basis of $r(O) = 1.40$ Å. The values revised by them (4) were not used, since the agreement between the calculated and the experimental results seems worse. For In, they gave 0.790 Å.

Here,

$$K(M, M') = K(M) + K(M'), \tag{7}$$

$$a(M, M') = \frac{K(M)a(M) + K(M')a(M')}{K(M) + K(M')}. \tag{8}$$

By the use of the experimentally determined lattice constants and $a(R)$ given in Table I, parameters in Eq. (6), $a(M, M')$ and $K(M, M')/K(R)$, are estimated by the least-square's fit and are tabulated in Table II. Only the ratio of the "elastic" constants can be determined, of course. The results of the calculation using these parameter values are compared with the experiments in Figs. 3 and 4 for the case of M = Fe and M = Ga, respectively. Agreement seems satisfactory, except several cases for the In compound. The case of Fe–Mg, which is omitted in Fig. 3, is discussed in Section 4.1. (See Table VII.) As for the Al-compound, this process was inapplicable, since only a few compounds have been synthesized.

According to Eq. (7), the difference between $K(\text{Fe}, M')$ and $K(\text{Ga}, M')$ should be a constant if the "elastic model" is valid. Table II shows that this is approximately

TABLE II

$K(M, M')/K(R)$ AND $a(M, M')$ FOR THE (1, 1) COMPOUNDS AND THE DIFFERENCE BETWEEN Fe AND Ga COMPOUNDS

	$K(M, M')/K(R)$			$a(M, M')$ (Å)		
M' \ M	Fe	Ga	(Fe–Ga)	Fe	Ga	(Fe–Ga)
Mg		0.767			3.214	
	(0.865)[a]	(0.767)		(3.274)	(3.214)	
Mn	1.267	0.828	0.439	3.388	3.318	0.070
Fe	0.428	0.487	−0.059	3.248	3.250	−0.002
	(0.585)	(0.487)		(3.332)	(3.250)	
Co	0.549	0.447	0.102	3.243	3.137	0.105
	(0.546)	(0.448)		(3.244)	(3.136)	
Cu	0.600	0.538	0.062	3.376	3.305	0.071
	(0.617)	(0.519)		(3.375)	(3.306)	
Zn	0.583	0.475	0.108	3.242	3.141	0.101
	(0.579)	(0.481)		(3.242)	(3.141)	

[a] Values in parentheses are calculated from Table IV. See the end of this section.

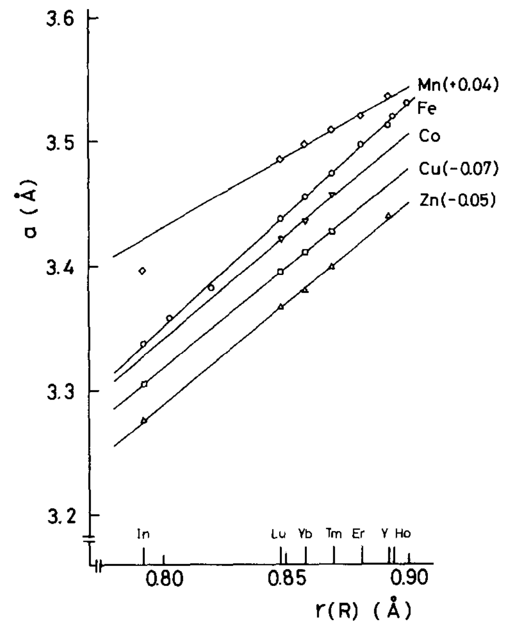


FIG. 3. The lattice constant a of $R\mathrm{Fe}M'\mathrm{O}_4$, as a function of the Shannon–Prewitt radii of R^{3+}. Points are the experimental data (*1*) and fine lines are calculated by Eq. (6) and parameters in Table II. Values for Mn, Cu, and Zn compounds are shifted vertically by the amount indicated in parentheses in the figure, to avoid confusion. Points for M' = Fe between In and Lu are for $\mathrm{In}_{0.8}\mathrm{Lu}_{0.2}\mathrm{Fe}_2\mathrm{O}_4$ and $\mathrm{In}_{0.5}\mathrm{Lu}_{0.5}\mathrm{Fe}_2\mathrm{O}_4$, respectively, and a point at $r(R)$ = 0.900 is for $\mathrm{Y}_{0.5}\mathrm{Dy}_{0.5}\mathrm{Fe}_2\mathrm{O}_4$.

verified for M' = Co, Cu, or Zn, but is not for M' = Mn and Fe.

Similar analysis can be adopted to the series of changing m with fixed M', which has been synthesized systematically only for Zn. Then,

$$a = \frac{K(R, M)a(R, M) + mK(M')a(M')}{K(R, M) + mK(M')}. \tag{9}$$

Expressions for $K(R, M)$ and $a(R, M)$ are the same with Eqs. (7) and (8) with the substitution of M' by R. In this case, however, experimental data show that Eq. (9) is valid only in a restricted range of m; i.e., the linear approximation of Eq. (1) is not good for the total series. We consider the compounds of smaller m, because parameters in this range can be compared with those of (1, 1) compounds. Determined parameter values are tabulated in Table III, and the calculated values are compared with the experiments in Figs. 5 and 6. As is shown, experimental data are smaller than the calculated values in the large m region of Tm or Yb compounds.

In the analysis shown in the figures, a(Zn), the limiting value of a for $m \to \infty$, was fixed as 3.250 Å, the value of würtzite-type ZnO. This was confirmed consistent by a preliminary analysis in which a(Zn) was treated as a parameter and determined to be 3.252 Å.

According to our assumption (iii), $K(R$, Fe) or $K(R$, Ga) should be identical irrespec-

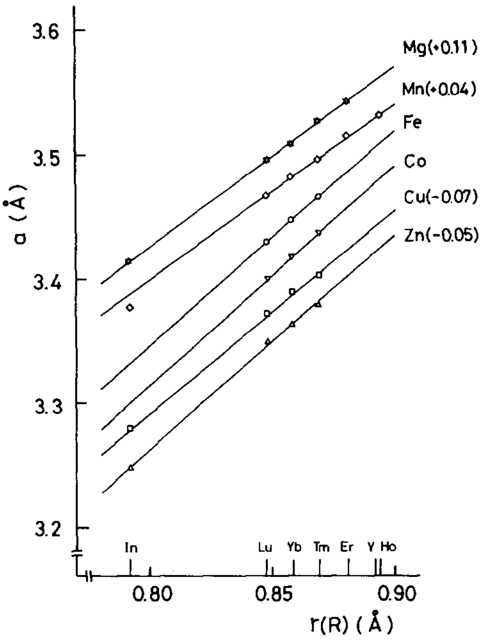


FIG. 4. The lattice constant a of $R\mathrm{Ga}M'\mathrm{O}_4$, as a function of the Shannon–Prewitt radii of R^{3+}. Points are the experimental data (*1*) and fine lines are calculated by Eq. (6) and parameters in Table II. Values for Mg, Mn, Cu, and Zn compounds are shifted vertically by the amount indicated in parentheses in the figure, to avoid confusion.

TABLE III

$K(R, M)/K(\mathrm{Zn})$ AND $a(R, M)$ FOR THE (1, m) Zn COMPOUNDS

R \ M	$K(R, M)/K(\mathrm{Zn})$ Fe	Ga	In	$a(R, M)$ (Å) Fe	Ga	In	Region of m used Fe	Ga	In
Yb	2.78	2.31		3.494	3.486		1–3	1–3	
	(2.67)	(2.44)		(3.501)[a]	(3.479)				
Lu	2.65	2.53		3.477	3.457		1–3	1–5	
	(2.67)	(2.44)		(3.479)	(3.455)				
In	2.69	4.66	2.10	3.356	3.311	3.507	1–10	1–7	3–9, 11
	(2.67)			(3.353)	(3.317)				
Sc	1.91			3.311			2–7		

[a] Values in parenteheses are calculated from Table IV.

tive of the rare-earth element. In the case of Fe compounds, this was proved except for R = Sc. For M = Ga, K(In, Ga) is too large compared with those for Yb or Lu. Furthermore, the change of a in $\mathrm{ScGaO_3(ZnO)}_m$ is not monotonous, though the amount is not so large. We ignore these cases in the following analysis and set $K(R, \mathrm{Fe})/K(\mathrm{Zn}) = 2.71$ and $K(R, \mathrm{Ga})/K(\mathrm{Zn}) = 2.42$, the average value for Yb, Lu and In compounds in the former and for Yb and Lu compounds in the latter.

We determined five parameters, K(Fe), K(Ga), K(Co), K(Cu), and K(Zn) from six $K(M, M')$ plus two $K(R, M)$, by least-squares fit. Then, $K(M' = \mathrm{Fe})$ and K(Mg) were also determined from K(Ga, Fe) and K(Ga, Mg). (See Section 4.5.) The results are tabulated in Table IV. $K(M, M')$ and $K(R, M)$ calculated from these values are compared with those determined from the experiments directly and shown in Tables II and III. Agreement seems rather good. $a(M)$ and $a(M')$ were calculated from $K(M)$ and $K(M')$ determined above and $a(\mathrm{Zn}) = 3.250$ Å. They are also tabulated in Table IV.

3. Consideration of c

Because triangular nets of atoms stack along the c axis, the lattice constant c is a sum of the contributions of the U block and the T layers. According to assumption (iii), the former part, c(U), can be estimated by Eq. (3):

$$c(\mathrm{U}) = 2\sqrt{(r(R) + r(\mathrm{O}))^2 - a^2/3}. \quad (10)$$

By a subtraction of this quantity from c, the contribution of the T layers is deduced. Of course, number of the U block in a unit cell

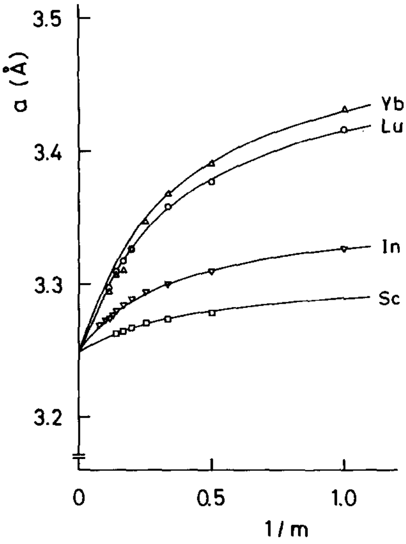


FIG. 5. The lattice constant a of $R\mathrm{FeO_3(ZnO)}_m$, as a function of $1/m$. Points designate the experimental data (*1*) and fine lines are calculated by Eq. (9) and parameters in Table III.

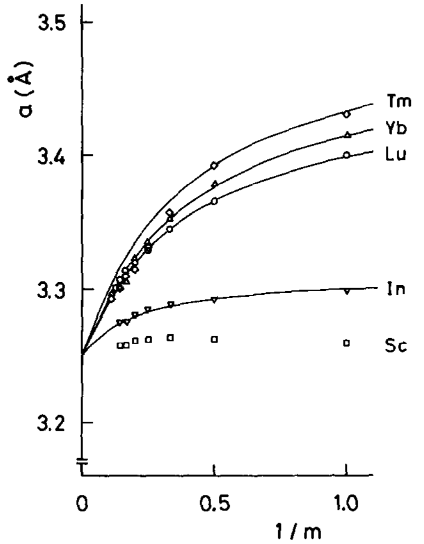


FIG. 6. The lattice constant a of $R\mathrm{GaO_3(ZnO)}_m$, as a function of $1/m$. Points designate the experimental data (*1*) and fine lines are calculated by Eq. (9) and parameters in Table III.

should be taken into account in the deduction. (See Fig. 2.) In the case of the (1, 1) compounds, $c/3 - c(\mathrm{U})$ is the contribution of double T layers. The average distance of the neighboring oxygen layers in the stacking of the T layers, $c(\mathrm{T})$, is one-third of this quantity:

$$c(\mathrm{T}) = (c/3 - c(\mathrm{U}))/3. \qquad (11)$$

As was already pointed out, c decreases with increasing a in a series of compounds with the same M and M' but different R. To make comparison between the compounds with different M or M', it should be better to normalize a by $a(M, M')$ and $c(\mathrm{T})$ by the value at $a = a(M, M')$. Figure 7 shows such a plot. As is seen, all the experimental data lies on a straight line, regardless of M or M', with the slope of -1.42,

$$\frac{c}{c(M, M')} = 1 - 1.42 \cdot \left(\frac{a}{a(M, M')} - 1\right), \qquad (12)$$

except at the larger end of a in some series. In the case of Ga–Mn compounds, a has a tendency to saturate, whereas c does in Ga–Co, Fe–Fe, Fe–Zn, Fe–Co, Ga–Cu, and Fe–Cu compounds. The limit of $a/a(M, M')$ for the linear relation between a and c is smaller for Fe compounds than for Ga, whereas that of c seems smaller for Ga compounds.

The normalization factors $c(M, M')$, or $c(\mathrm{T}; M, M')$ at $a = a(M, M')$, are tabulated in Table V. Differences between M = Fe and Ga are also shown in the table. Once more, the Fe–Fe compound is an exception.

For the compounds of m larger than 1, such a plot is not possible because experimental data for the compound with large m are not available except for M' = Zn. Moreover, as is seen in Figs. 5 and 6, assumptions (i) and (ii) are not good for larger m and R's of large ionic radius. Nevertheless, qualitative characteristics can be deduced mainly from In and Lu compounds. Figure 8 is the m-dependence of $c(\mathrm{T})$ for

TABLE IV

$K(M)/K(R)$, $K(M')/K(R)$, $a(M)$, AND $a(M')$, ESTIMATED FROM THE DATA IN TABLES II AND III

M	$K(M)/K(R)$	$a(M)$ (Å)	M'	$K(M')/K(R)$	$a(M')$ (Å)
Fe	0.149	3.219	Mg	0.716	3.285
Ga	0.051	2.222	Fe	0.436	3.370
			Co	0.397	3.254
			Cu	0.468	3.425
			Zn	0.430	3.250

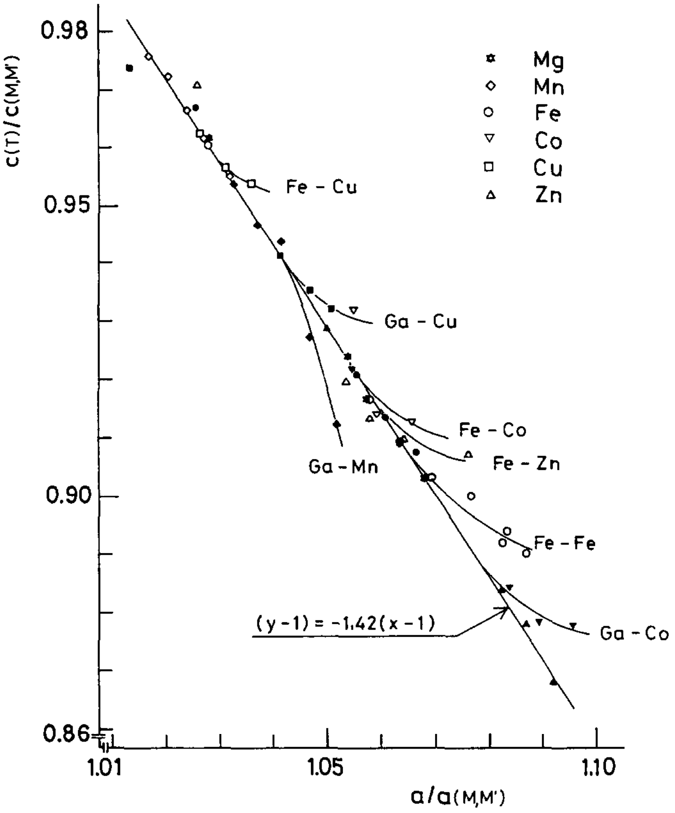


FIG. 7. The normalized dimension of the T layer of (1, 1) compounds along the *c* axis, *c*(T), as a function of *a* normalized by *a*(*M*, *M'*). Points designated experimental data (*l*) and fine lines are guides for the eyes. The normalization factors, *c*(*M*, *M'*), are tabulated in Table V.

both series of M = Fe or Ga and M' = Zn. Though lack of sufficient number of data restricts quantitative discussion on the dependence of c on a, negative slope (see Fig. 7) seems to become steeper with increasing m. Fortunately, this ambiguity does not make so much trouble in the estimation of c(T), since $a \simeq a(M, m\text{Zn})$ in these compounds. Here, $a(M, m\text{Zn})$ is the normalization factor for a of the (1, m) compounds

TABLE V

$c(M, M')$, NORMALIZATION FACTORS FOR THE c(T) OF (1, 1) COMPOUNDS, IN (Å)

M' \ M	Fe	Ga	(Fe–Ga)
Mg		2.234	
Mn	2.203	2.262	−0.059
Fe	2.292	2.284	0.009
Co	2.275	2.340	−0.065
Cu	2.081	2.121	−0.040
Zn	2.271	2.346	−0.075

which was calculated from $K(M)$, $K(\mathrm{Zn})$, $a(M)$, and $a(\mathrm{Zn})$, tabulated in Table IV, as

$$a(M, m\mathrm{Zn}) = \frac{K(M)a(M) + mK(\mathrm{Zn})a(\mathrm{Zn})}{K(M) + mK(\mathrm{Zn})}. \quad (13)$$

In Fig. 8, fine lines are those similar to Eq. (9),

$$c(\mathrm{T}; M\,m\mathrm{Zn}) = \frac{C(M)c(M) + mC(\mathrm{Zn})c(\mathrm{Zn})}{C(M) + mC(\mathrm{Zn})}, \quad (14)$$

with $c(\mathrm{Zn}) = 2.603$ Å, $c(\mathrm{Fe}) = 2.071$ Å, $c(\mathrm{Ga}) = 2.233$ Å, $C(\mathrm{Fe})/C(\mathrm{Zn}) = 1.72$ and $C(\mathrm{Ga})/C(\mathrm{Zn}) = 2.94$. It is to be noted that $c(\mathrm{Zn}) = 2.603$ Å was assumed as one-half of the lattice constant c of würtzite, after the confirmation of the consistency.

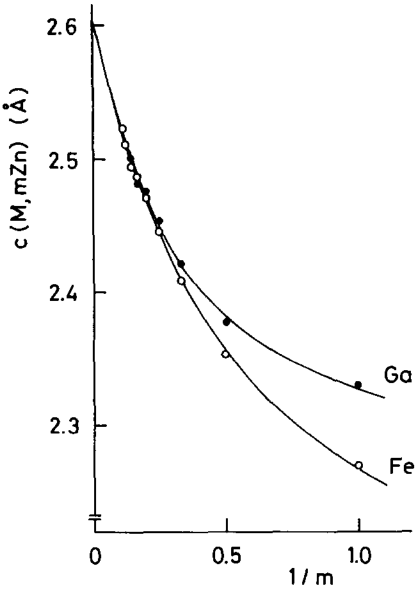


FIG. 8. Normalization factor of $c(\mathrm{T})$ of (1, m) Zn compounds, $c(\mathrm{T}; M, m\mathrm{Zn})$, for M = Fe and M = Ga. Points designate the experimental data and fine lines are calculated by Eq. (14).

4. Discussion

4.1. On the Evaluation of Experimental Data

The main problem of the experimental data is supposed to arise from the specimen. In general, the stoichiometry plays an important role in determining the physical properties of $R\mathrm{Fe_2O_4}$. They are Berthollides existing in the region extending mainly to the oxygen-deficient side in the phase diagram.

A few reports have been made on the lattice constants of the same compounds with different oxygen content. See Table VI. The lattice constants of $\mathrm{YFe_2O_{4+x}}$ do not depend on x so much in the region $0.00 > x > -0.09$. On the other hand, a of $\mathrm{YbFe_2O_{4+x}}$ decreases by 0.005 Å or 0.15% with an increase of x by about 0.04. In some cases, much larger differences, up to about 1% for $\mathrm{LuGaMgO_4}$, e.g., were reported for the same compound synthesized at different laboratories. Such a difference might be attributed to the different conditions of reactions in the synthesis.

(1, 1) compounds of Fe and Mg can be considered to give another example. Lattice constants from $\mathrm{ErFeMgO_4}$ to $\mathrm{LuFeMgO_4}$ are tabulated in Table VII. The values in parentheses are those estimated from other compounds by Eqs. (2), (10), and (12) using parameter values in Tables IV and V. Differences between the measured and the estimated values of Yb and Lu compounds are not so large. Both a and c of Er and Tm compounds are, however, too large to be accounted for by the linear extrapolation from other compounds. Note that both a and c are larger in Er and Tm compounds than in Yb and Lu compounds, in contrast to the common feature, as shown in Fig. 7. In order to synthesize Fe–Mg compound from $R_2\mathrm{O_3}$, $\mathrm{Fe_2O_3}$, and MgO powders in air or $\mathrm{O_2}$ gas, we have to heat the mixture at much higher temperatures than those for other compounds. We cannot neglect the possibility of introduction of $\mathrm{Fe^{2+}}$ ions or nonstoichiometry in the Fe–Mg compound (*10*).

TABLE VI

DEPENDENCE OF LATTICE CONSTANTS ON STOICHIOMETRY

	x	a (Å)	c (Å)	Reference
YFe_2O_{4+x}	0.00	3.513	24.78	(*5*)
	−0.095	3.513	24.76	
$YbFe_2O_{4+x}$	−0.027	3.4621(4)	25.126(6)	(*6*)
	−0.003	3.4596	25.117	
	+0.015	3.4570	25.121	

4.2. On the Dimension of the U Block: Rigid-Sphere Approximation and the Site Preference

Close packing of spherical ions is a widely accepted model of ionic crystals, though the limitations are also discussed. Prewitt argued that ions should be considered as composed of small relatively hard cores separated by the regions with much lower electron density of about 0.4 Å (*11*). Atomic compressibility is accomodated in the latter part. For the discussion of a in the present report, the rigid-sphere approximation was used to estimate the size of the coordination octahedron of R in the free state, i.e., without "external" stress. "Rigidity" is not necessary there. Systematic dependence of the lattice constants on R seems to show that the estimated $a(R)$, and the assumption of identical $K(R)$ might not be so bad for rare earths and Y. As for c(U), however, the assumption plays an essential role.

The validity of the rigid-sphere approximation can be examined for the compounds for which atomic positions have been determined. Reported atomic distances between R and coordinating O are compared with the sum of the ionic radii in Table VIII. c(U) and the distance of oxygen in the different c planes of the U block are also tabulated. Measured R–O distances coincide with the sum of the ionic radii in In compounds, but the experimental value becomes smaller with increasing ionic radius, up to about 1% in YFe_2O_4. (The case of $Eu_{0.5}Yb_{0.5}Fe_2O_4$ is discussed in the next subsection.) c(U), too, does not show good coincidence. Dependence of this quantity on $r(R)$ is reversed.

It is interesting to note that the distance of O in the different c planes in a U block is almost identical for all compounds, ≈2.87 Å. If we set this value, c(U) can be calculated from experimentally determined a by

$$c(\mathrm{U}) = \sqrt{2.87^2 - a^2/3}. \qquad (15)$$

As is shown in the table, Eq. (15) gives a better estimate of c(U) than that of the rigid-sphere approximation.

If we adopt Eq. (15) to all the compounds, parameters tabulated in Table V, c(T), etc., change. The difference between c(Fe, M′) and c(Ga, M′) for the same M', the fourth column, distributes between −0.040 and −0.049 Å except M' = Fe. The arguments in Section 3, however, need not be changed qualitatively. The largest change in the parameter values is for the slope of the plot in Fig. 7 and Eq. (12): from −1.42 to −0.985.

Another point to be made here is the location of In and Sc. Recently, crystal chemical study of this series of compounds was extended to $In_{1-x}Fe_{1+x}O_3 \cdot (ZnO)_m$ and $In_{1-x}Ga_{1+x}O_3 \cdot (ZnO)_m$. It was disclosed that the region of this type of compound extends not only to the negative side of x (*17, 18*) but also to the positive side when m is sufficiently large (*19*). In and Fe or Ga can interchange their location not only in the T layers but also in the U blocks. In the case of In–Al–Zn system at 1350°C, no stoichio-

TABLE VII

LATTICE CONSTANTS OF (1, 1) COMPOUNDS OF Fe AND Mg

R	a (Å)	c (Å)	Reference
Er	3.521	25.69	(*8*)
	(3.450)[a]	(24.74)	
Tm	3.503	25.55	(*8*)
	(3.433)	(24.84)	
Yb	3.429	25.16	(*8*)
	3.425	25.11	(*7*)
	3.422	25.16	(*9*)
	(3.418)	(24.93)	
Lu	3.428	25.31	(*8*)
	3.415	25.25	(*7*)
	(3.405)	(25.00)	

[a] Values in parentheses are calculated from Tables IV and V, and Eqs. (2), (10), and (12).

metric compound but only with negative x exists for $2 < m < 6$ (*20*). It is natural to consider that the site preference of In^{3+} is not complete even for $x = 0$, nominally stoichiometric compound. This will partly explain the deviation of the In–Mn compounds in Figs. 3 and 4.

As for Sc^{3+}, a of $ScGaM'O_4$ (M' = Mg, Cu, or Zn) corresponds to $r(R) = 0.76$–0.77 Å on the curves in Fig. 4. This is much larger than the Shannon–Prewitt radius of Sc^{3+} coordinated by six O^{2-}, 0.730 Å. Since the ionic radius of M and M' is still smaller (Ga^{3+}: 0.620 Å; Mg^{2+}: 0.720 Å; Cu^{2+}: 0.73 Å; Zn^{2+}: 0.745 Å) except Zn^{2+}, substitution of Sc in the U layer by M or M' will result in the decrease, instead of increase as observed, of a. Deviation of the lattice constants in the Sc compounds might not be explained by the imperfect preference of Sc in the U layer. Chemical consideration, too, does not support the location of Sc^{3+} ions in the T layer, akin to tetrahedrally coordinated site (see below). We have no idea at present to account for the deviation in this case.

4.3. On the "Elastic" (Linear) Approximation

Consideration of the strains in the bond length, resulting from the constraints to form a crystal, is not seldom. For example, Brown discussed recently the relation between superconducting transition temperature and the charge transfer between Cu atoms induced by the change of the bond length in $Ba_2YCu_3O_x$ (*21*). He concluded that there can be residual internal strains,

TABLE VIII

COMPARISON BETWEEN THE EXPERIMETAL AND CALCULATED ATOMIC DISTANCES IN THE U BLOCK

	Atomic distance, R–O		c(U)				
Compound	Exp.	Calc. (1)[a]	Exp.	Calc. (1)[a]	Calc. (2)[b]	O–O[c]	Reference
$InAlCuO_4$	2.189	2.192	2.140	2.152	2.142	2.87	(*12*)
$InFe_{1.75}Si_{0.25}O_4$	2.188	2.192	2.145	2.162	2.145	2.870	(*12*)
$YbFe_2O_4$	2.241	2.258	2.046	2.116	2.063	2.856	(*13*)
$Eu_{0.5}Yb_{0.5}Fe_2O_4$	2.268	2.304	2.090	2.243	2.046	2.901	(*14*)
		(2.275)		(2.121)			
YFe_2O_4	2.269	2.292	2.030	2.128	2.029	2.870	(*15*)
$LuFe_2O_4$	2.237	2.248	2.059	2.105	2.071	2.861	(*16*)
$LuFeCoO_4$	2.230	2.248	2.075	2.153	2.084	2.865	(*16*)

[a] Calculation on the rigid sphere model of the anions and cations. Values for $Eu_{0.5}Yb_{0.5}Fe_2O_4$ are the arithmetic average of the cases of R = Eu and R = Yb and those for $r(R) = 0.875$ Å (in parentheses).

[b] Calculation on the assumption that O–O distance within the U block is 2.87 Å, using observed a.

[c] Atomic distance between oxygen ions in the neighboring c planes within a U block.

stretched Ba–O and compressed Cu–O, that are not relaxed by charge transfer. In such cases, a linear approximation with fixed parameter values will not work. Figures 3–6 show several examples in the present analysis. Here, we add two more examples of inapplicability, in order to know the region where the "elastic" or the extended Vegard's model is valid.

The first example is $Eu_{0.5}Yb_{0.5}Fe_2O_4$. a of this compound was reported 3.486 Å, which corresponds to $r(R) = 0.875$ Å in Fig. 3 (*14*). This value should be compared with 0.904 Å, the average of Eu^{3+} and Yb^{3+}. On the present assumptions, $a(R)$ for mixed R elements should be the weighted mean, since $K(R)$ is identical: ordinary Vegard's law should be fulfilled here. Note that $a(R)$ can be considered as a linear function of $r(R)$ in this region. In contrast to the Eu–Yb case, linear interpolation of $r(R)$ gives reasonable results in the case of the elements with a smaller difference in the ionic radius, e.g., In–Lu or Y–Dy (*7*). They were shown in Fig. 3. It seems reasonable that the small difference guarantees linear interpolation.

The second example is the case of M' = Mn. In this case, the value of K as well as the difference between K(Fe, Mn) and K(Ga, Mn) (Table II) is much larger than that in the other compounds. On the other hand, differences in $a(M, \mathrm{Mn})$ and $c(M, \mathrm{Mn})$ are normal. Though a and c themselves can be accounted for by the present model, the value of parameter K should not be considered constant for changing M. The case of M = Ga seems similar. Both K and a in Table IV are too small to be realized, suggesting that the validity of the values is limited.

4.4. On the Dependence of c on a

Let us note first that c(T) is not the dimension of one T layer along the c axis but the average distance between oxygen layers other than in the U block. Since c(T) increases with increasing m and tends to that of würtzite, and since the normalized c(T) in the (1, 1) compound is not dependent on the transition element but only on the normalized a, it seems plausible to assume that the increase of c(T) for smaller a is mainly due to the shift of cation and anion layers composing one T layer, along the c axis. Two triangular nets of $M + M'$ and O do lie on the same c plane only if that is forced to by the symmetry of the crystal, i.e., in the T layer just at the center of two U blocks which appears when $n + m$ is odd. In würtzite, of course, they are on the different c plane making the coordination polyhedron of M' a tetrahedron, rather than the trigonal bipyramid in the present crystal. It is natural that the anion–anion distance decreases along the c axis, whereas it increases within the c plane, when cations want to locate at the center of the anion triangles. The common feature shown in Fig. 7 suggests the common nature of the coupling of cations and anions. Figure 8 and Eq. (14) indicate the affinity between the tetrahedral and trigonal bipyramidal coordination.

In this context, three points are to be made.

(1) Synthesis of (1, m) compound is much harder for even m compared to odd, when m becomes large. This can be either the elongation of time for the solid reaction or the instability of the compound. At any rate, cohesive energy of (m = even) compounds decreases for increasing m faster than that of (m = odd) compounds. As is stated above, there is a T layer composed of $M + M'$ and O nets on the same c plane when m is even. We can expect that the lower limit of a is larger in such a T layer compared to other T's. On the other hand, large m makes a smaller usually. This conflict will destabilize the crystal.

(2) Lack of the linear relation between c(T) and a at the large-a end of the (M, M') compounds (Fig. 7) can be naturally explained as a phenomenon when $M + M'$ and O nets lie in nearly the same c plane. In

such a case, further decrease of c will not result by the increase of a.

(3) The thermal-expansion coefficient of $LuFe_2O_4$ along the c axis is negative above room temperature, whereas that of YFe_2O_4 does not show any anomaly (*22*). When the negative relation exists between c and a, thermal expansion along the a axis will cause shrinkage along the c. This is the case of $LuFe_2O_4$. YFe_2O_4 deviates from the principal line in Fig. 7 and no anomaly can be expected.

4.5. *On the Anomaly of the Fe–Fe Compound*

It is evident in the tables that the differences of all parameters are anomalous between Fe–Fe and Ga–Fe compounds. This should be due to the peculiarity of the electronic state in the Fe–Fe compound, in which the average valence of Fe is 2.5+. There are two ionic states of Fe, though not strictly 2+ and 3+, in a crystallographically equivalent site. Charge fluctuation between them, the frequency of which is about 10 MHz at room temperature, was observed in Mössbauer spectrum directly (*22*). At the same time, the isomer shift of the higher valence state in RFe_2O_4 deviates from those in the compounds with other M' (*22*). Rather low electrical resistivity, of the order of 1 Ω · cm at room temperature, is also attributed to the charge fluctuation. In the case of stoichiometric YFe_2O_4 or $ErFe_2O_4$, a Verwey-type tansition was discovered (*23, 24*).

We conclude that not the Ga–Fe but the Fe–Fe compound is anomalous in the present analysis of lattice constants. This is another evidence of the effect of the charge fluctuation, or the existence of the charge density waves, in this crystal. Below the Verwey transition, where charge fluctuation stops, a increases (*25*). Charge flucuation or the transfer of electrons, which takes place mainly within a T layer, is expected to favor shorter a, and forces c to expand.

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