An elastic block model for the relationship between the composition and the cell volume in the humites

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ABSTRACT

The relationship of the cell volume to the composition of humite solid solution, $x\text{Mg}(\text{OH})_2 \cdot (1-x)\text{MgF}_2 \cdot n\text{Mg}_2\text{SiO}_4$ ($0 \leq x \leq 1$ and $n=1, 2, 3$ and 4) was formulated on the basis of the following model: The crystal of the humites is composed of small elastic blocks consisting of end member units, which have the different volume in the pure end members. Each block is constrained to have the same volume in the solid solution, and the strain energy is then stored in each block. The minimization criterion of the total strain energy is introduced to determine the equilibrium cell volume of the solid solution. The calculated cell volumes on this model agree with the observed values up to four figures for all the data available. Application of the present solid solution model is extended to cover the cation substitution in the humites and also to the solid solutions of alkali halide.

Introduction

The humite group consists of four minerals and has the general formula, $x_1\text{M}(\text{OH})_2 \cdot x_2\text{MF}_2 \cdot x_3\text{TiO}_2 \cdot n\text{M}_2\text{SiO}_4$ where $x_1+x_2+x_3=1$ and $n=1, 2, 3$ and 4 and where M is Mg, Fe, Mn, Ca, Zn in decreasing order of abundance (Jones *et al.*, 1969). If $n=1$, the mineral is norbergite, if $n=2$ it is chondrodite, if $n=3$ it is humite and if $n=4$ it is clinohumite. The general formula was determined by Jones *et al.* (1969) on the basis of the crystallographic and crystal-chemical evidences that Ti replaces Mg according to the relation $\text{Ti}+2(\text{O}) \rightleftharpoons \text{Mg}+2(\text{OH}, \text{F})$

with little effect on the cell volume and occupies the octahedral sites. Recently these minerals have been suggested as hydrous minerals in the upper mantle (McGechin *et al.*, 1970; Ringwood, 1975, 1976; Aoki *et al.*, 1976; Akimoto *et al.*, 1977; Yamamoto and Akimoto, 1977).

Taylor and West (1928, 1929) determined the crystal structures of the humite group which were based on a hexagonal close-packed array of anions similar to that of forsterite. Norbergite and humite have the orthorhombic symmetry, $Pbnm$, and others the monoclinic, $P2_1/b(\alpha \text{ obtuse})$. The setting, $P2_1/b$, is usually employed for chondrodite and clinohumite because it permits direct comparison of their cell parameters and crystal structures with those of norbergite, humite and forsterite. The humites and forsterite have the following lattice parameters: $a \sim 4.7 \text{ \AA}$, $b \sim 10.2 \text{ \AA}$ and $c \cdot \sin \alpha \sim 1.49m \text{ \AA}$, where $m=6$ for norbergite, $m=5$ for chondrodite, $m=14$ for humite, $m=9$ for clinohumite and $m=4$ for forsterite. The basal plane of the hexagonal close-packed array of anions is parallel to (100). The crystal structures of the humites consists of alternate slabs parallel to (001) which have the forsterite-like structure and brucite-like structure (Taylor and West, 1928, 1929; Bragg and Claringbull, 1965; Ribbe *et al.*, 1968).

Ribbe *et al.* (1968) found that normalized cell volume (normalized to one half the mean anion-anion distance along the normal to (001), namely $abc \cdot \sin \alpha / m$) in the series, forsterite-fluor-humite-norbergite, decreased linearly with increasing F/O ratio. They explained that this was primarily due to the substitution of smaller F for O and secondarily due to the decrease in polyhedral distortions caused by the increased substitution of tetrahedral voids for tetrahedrally coordinated Si and the concomitant decrease in the number of shared polyhedral edges. According to their reasoning, the normalized cell volume in the series, forsterite-hydroxyl-humites, should decrease with increasing OH/O ratio. But the normalized cell volumes calculated from the unit cell volumes of hydroxyl-clinohumite and hydroxyl-

chondrodite (phase D in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$) determined by Yamamoto and Akimoto (1974, 1977) are larger than that of forsterite and increase with increasing OH/O ratio. There must be the tertiary process to determine the normalized cell volumes in the humites and forsterite.

The normalized cell volumes of the natural humites whose compositions have been analyzed using the microprobe analysis techniques by Jones *et al.* (1969) fall between those of the corresponding both end members. The linear relationship of either the cation radius (r) or volume (r^3) to the unit cell volume of isostructural series with a constant anion is well known (Shannon and Prewitt, 1969). However, similar relationship does not hold for the anion radius and the normalized cell volume in the humites. A new model for interpreting the relationship of the anion composition and the normalized cell volume in the humites is necessary.

The present work was intended to formulate the relationship of the anion composition to the cell volume in humites on the basis of the following model: (1) The crystal of the humites is composed of small blocks. Each block consists any of the formula units, $\text{M}(\text{OH})_2 \cdot n\text{M}_2\text{SiO}_4$, $\text{MF}_2 \cdot n\text{M}_2\text{SiO}_4$ or $\text{TiO}_2 \cdot n\text{M}_2\text{SiO}_4$. (2) Each block is regarded as an elastic body, and it is constrained to have the same volume in the crystal of solid solution. (3) The strain energy of a block is proportional to square of dilatation (or compression). (4) The proportional coefficients were assumed to be adjusting parameters in this theory. (5) The volume of the unstrained block was estimated by the crystallographic data of the end materials. (6) The normalized cell volume of the crystal under consideration is determined from the condition that the total strain energy of all blocks in the crystal is minimum.

The elasticity of a crystal can, in principle, be expressed by the appropriate derivatives of the lattice energy function. The lattice energy can be expressed by the sum of the potential energies of all

ions in the field of inter-ionic forces. Then, it is possible to distribute the lattice energy to blocks in the crystal. The inter-ionic forces can be classified into three types; (1) Long range force (Madelung force). The nature of this force is independent of the species of blocks. (2) Short range forces between ions within a block. These forces are proper to the species of blocks. (3) Short range forces between ions which belong to different blocks each other. These forces depend upon the species of block pairs. If it is assumed that the dependence of the third forces upon the species of block pairs can be effectively neglected, the lattice energy of a block is defined independently of the environmental blocks and thus of the composition of the whole crystal. Then, the elasticity of a block is regarded to be equivalent to that of the corresponding end materials. The present theoretical model is based on this assumption.

*Theory for the elastic relationship of the composition
and the cell volume in the humites*

In order to calculate the normalized cell volume, the formula of a humite group crystal is represented by

$$x_1A_1 \cdot x_2A_2 \cdot x_3A_3 \cdot nB, \quad (1)$$

where A_1 , A_2 , A_3 and B stand for $M(OH)_2$, MF_2 , TiO_2 and M_2SiO_4 , respectively, and where

$$x_1 + x_2 + x_3 = 1 \quad (2)$$

and $n=1, 2, 3$ and 4 . It has to be noted that n expressed not only the kind of mineral but also the ratio, (number of four coordinated O^{2-})/(twice the number of three coordinated anions). For the octahedral cation, an average radius, $\bar{r}$, is assumed. We suppose that the crystal can be virtually divided into small blocks so that each has any of the compositions, $A_i \cdot nB$, where $i=1, 2$ or 3 , and has the average radius, $\bar{r}$, of the octahedral cation. Further, each block is

stressed when the blocks are different in composition, so that all blocks have the same normalized cell volume, V' . If we express the deformation energy per normalized cell of $A_i \cdot nB$ blocks by ϕ_i , the total strain energy, E , of all blocks in the crystal having the formula (1) is

$$E = N \sum_{i=1}^3 x_i \phi_i, \quad (3)$$

where N is the number of normalized cells in the crystal. If we suppose that the block is an elastic body and is hydrostatically stressed and its strain energy is proportional to square of dilatation (or compression), ϕ_i are given by

$$\phi_i = (1/2) k_i V_i \theta_i^2, \quad (i=1, 2 \text{ and } 3) \quad (4)$$

where θ_i are dilatation and

$$\theta_i = (V' - V_i) / V_i \quad (5)$$

and where $V_i(n, \bar{r})$ is the normalized cell volume of a crystal having the end-composition, $A_i \cdot nB$, in which cells are unstressed, and $k_i(n, \bar{r})$ is the isothermal bulk modulus (the reciprocal of the volume compressibility) of the $A_i \cdot nB$ block. (The parameters, x_1, x_2, x_3, n and $\bar{r}$, are omitted when there is no possibility for confusion.)

When x_1, x_2, x_3, n and $\bar{r}$ are given, the actual normalized cell volume, $V(x_1, x_2, x_3, n, \bar{r})$, satisfies the condition that the strain energy is a minimum, then

$$[dE/dV']_{V'=V} = 0. \quad (6)$$

We obtain the following relation between the composition and the normalized cell volume, from eqs. (3), (4), (5) and (6),

$$V(x_1, x_2, x_3, n, \bar{r}) = \left\{ \sum_{i=1}^3 x_i k_i(n, \bar{r}) \right\} / \left\{ \sum_{i=1}^3 x_i k_i(n, \bar{r}) / V_i(n, \bar{r}) \right\}. \quad (7)$$

Next, we shall examine the dependence of the normalized cell volume, V , upon the average radius of the octahedral cation, $\bar{r}$,

based on a linear approximation. From the differentiation of both sides in eq. (7), we obtain the following relation between the increments, $\Delta\bar{r}$ of $\bar{r}$ and ΔV of V ;

$$\Delta V = \Delta\bar{r} \cdot \left[\sum_{i=1}^3 (x_i k_i / V_i) \{1 + (V - V_i) / V_i\} (dV_i / d\bar{r}) \right] / \left[\sum_{i=1}^3 (x_i k_i / V_i) \right], \quad (8)$$

where the bulk moduli, k_i , are assumed to be constant during a slight variation of $\bar{r}$. Since ΔV concerned is a small correction term in our calculation, we may use a crude approximation that the quantities, $dV_i / d\bar{r}$, take a common value A for all species of anion, namely

$$dV_i / d\bar{r} \equiv A. \quad (9)$$

Then we obtain

$$\Delta V \cong A \cdot \Delta\bar{r}, \quad (10)$$

where A generally depends upon n and r_0 . Under the condition of eq. (9), eq. (10) means that V is expressed by the sum of two terms: One depends upon the composition of the three-coordinated anion site, and the other upon the average radius of the octahedral cation. Namely, in full notation,

$$V(x_1, x_2, x_3, n, \bar{r}) = V(x_1, x_2, x_3, n, r_0) + A(n, r_0) \cdot \Delta\bar{r}, \quad (11)$$

where

$$\Delta\bar{r} = \bar{r} - r_0 \quad (12)$$

Procedure of calculation and results

The available data of the normalized cell volume and the composition in natural humites are limited to those reported by Jones *et al.* (1969). The normalized cell volume, V_{obs} , the composition, x_1 , x_2 and x_3 , and the deviation, $\Delta\bar{r}$, of the average radius of the octahedral cation from the radius of Mg^{2+} ($0.720\text{\AA}$) in the natural humites reported by them, except boron containing chondrodite (Hinthorne and Ribbe, 1973), are listed in Table 1 together with those of end-

Table 1. Observed and reduced normalized cell volume and some parameters relating to the calculation.

Mineral and number	<i>n</i>	OH <i>x</i> ₁	F <i>x</i> ₂	OTi <i>x</i> ₃	<i>x</i>	$\Delta\bar{r}$ ($\times 10^{-3}\text{\AA}$)	<i>V</i> _{obs} * ($\text{\AA}^3$)	<i>V</i> _{red} * ($\text{\AA}^3$)	Reference
Norbergite 1	1	0.087	0.902	0.011	0.098	0.16	70.540 (4)	70.525 (4)	1
Chondrodite 2	2	0.366	0.633	0.001	0.367	0.52	71.859 (5)	71.811 (7)	1
Chondrodite 24	2	0.449	0.530	0.021	0.470	2.59	72.242 (?)	72.005(26)	1
Humite 3	3	0.406	0.393	0.201	0.607	-0.40	72.396 (3)	72.433 (5)	1
Humite 7	3	0.464	0.530	0.006	0.470	3.05	72.436 (2)	72.157(31)	1
Clinohumite 7	4	0.463	0.520	0.017	0.480	3.20	72.517 (5)	72.224(32)	1
Clinohumite 10	4	0.526	0.000	0.474	1.000	0.40	72.982(20)	72.946(20)	1
End-members									
F-norbergite	1	0	1	0	0	0	70.37 (2?)		2
F-humite	3	0	1	0	0	0	71.78 (4?)		2
OH-chondrodite	2	1	0	0	1	0	73.74 (2)		3
OH-clinohumite	4	1	0	0	1	0	73.01 (1)		4

Reference: 1; Jones, Ribbe and Gibbs (1969), 2; Van Valkenburg (1961),

3; Yamamoto and Akimoto (1974), 4; Yamamoto and Akimoto (1977).

* Estimated standard deviations are given in parentheses and refer to the last digit.

members reported by Van Valkenburg (1961) and Yamamoto and Akimoto (1974, 1977). Shannon and Prewitt's (1969, 1970) ionic radii are used. The radius of Mg^{2+} employed as r_0 in eqs. (11) and (12) because the average radii of the octahedral cations in the humites listed in Table 1 are close to the radius of Mg^{2+} . The normalized cell volumes of humite minerals whose compositions are known can be calculated by eqs. (7), (11) and (12), provided that $k_i(n)$, $V_i(n)$ and $A(n)$ are known. However, all those constants are not determined directly from available data. Then, some values were estimated under the following five approximations. (The assumptions in this paragraph are called approximations, in order to distinguish them from those in theoretical model.) Hereafter, the subscripts, 1, 2 and 3, of V_i and k_i are written by OH, F and O_{Ti} , respectively.

Approximation (i) on V_{OTi} and k_{OTi} : The data for the end-members, $\text{TiO}_2 \cdot n\text{M}_2\text{SiO}_4$, were not obtained and the contents of $\text{TiO}_2 \cdot n\text{M}_2\text{SiO}_4$ in the samples listed in Table 1 are low, except for clinohumite 10 (titano-clinohumite). Then, V_{OTi} and k_{OTi} in eq. (7) were, as an approximation, regarded to be equal to V_{OH} and k_{OH} , respectively, because the normalized cell volume of clinohumite 10 (Table 1) is approximately equal to that of hydroxyl-clinohumite and because the effective radius of OH in chondrodite ($1.45_8 \text{ \AA}$; Yamamoto, 1977) is close to that of three-coordinated O^{2-} . The approximation $k_{\text{OTi}} = k_{\text{OH}}$, was used for convenience' sake. According to these approximations, eq. (7) becomes

$$V(r_0) = \frac{V_{\text{F}}(r_0) \{1 - x(1 - K)\}}{1 - x \{1 - K \cdot V_{\text{F}}(r_0)/V_{\text{OH}}(r_0)\}}, \quad (13)$$

where

$$x \equiv x_1 + x_3 \quad (\text{then } x_2 = 1 - x) \quad (14)$$

and

$$K(n, r_0) \equiv k_{\text{OH}}(n, r_0)/k_{\text{F}}(n, r_0). \quad (15)$$

It is noted that eq. (13) is exact for Ti-free samples.

Approximation (ii) on V_F : According to Ribbe *et al.* (1968), the normalized cell volumes of fluor-end-members, $V_F(r_0)$, are expressed as

$$V_F(r_0) = V_0 - 2.12/n, \quad (\text{\AA}^3) \quad (16)$$

where V_0 is the normalized cell volume of forsterite ($72.49 \text{\AA}^3$).

Approximation (iii) on V_{OH} : The normalized cell volumes of hydroxyl-end-members, $V_{OH}(r_0)$, are expressed by eq. (17), in the cases of chondrodite ($n=2$) and clinohumite ($n=4$).

$$V_{OH}(r_0) = V_0 + 1.66/n + 1.68/n^2. \quad (\text{\AA}^3) \quad (17)$$

This relation was used for norbergite ($n=1$) and humite ($n=3$), because the hydroxyl-end-members of these minerals had never been reported previously in the literature.

Approximation (iv) on A : Ribbe *et al.* (1968) recognized the linear relations of the average radius of the octahedral cation to the normalized cell volume in olivines and humites, using Ahrens' (1952) ionic radii. If we use Shannon and Prewitts' (1969, 1970) ionic radii, the relation for the olivines is improved and expressed by

$$V_{\text{olivine}}(\bar{r}) = V_0 + 91.6 \cdot \Delta\bar{r}. \quad (\text{\AA}^3) \quad (18)$$

The formulations of the relations in humites are difficult because the normalized cell volume of humites depends not only upon the average radius of the octahedral cation but also upon the composition of the three-coordinated anion site as shown in eq. (11) and because the number of the data on humites is not enough. Then, the same equation as eq. (18) was assumed to be applicable to the humites, namely

$$A(n, r_0) = 91.6. \quad (\text{\AA}^2) \quad (19)$$

This assumption is justified by a diagram similar to figure 4 of Ribbe *et al.* (1968) and on the smallness of $\Delta\bar{r}$ listed in Table 1. The observed volume, V_{obs} , listed in Table 1 was corrected according to eqs. (11) and (19) and reduced to V_{red} which was the normalized cell

volume when $\bar{r}=r_0$.

$$V_{\text{red}} \equiv V(r_0) = V_{\text{obs}} - 91.6 \cdot \Delta \bar{r}. \quad (\text{\AA}^3) \quad (20)$$

The value of V_{red} is also listed in Table 1.

Approximation (v) on K : Since no data to estimate $K(n, r_0)$ in eq. (13) was available, it was determined as an adjusting parameter. $K(n, r_0)$ was calculated by eq. (21) which was equivalent to eq. (13).

$$K(n, r_0) = \frac{(1-x) \{V_{\text{red}} - V_{\text{F}}(n, r_0)\} V_{\text{OH}}(n, r_0)}{x \{V_{\text{OH}}(n, r_0) - V_{\text{red}}\} V_{\text{F}}(n, r_0)}. \quad (21)$$

This result is listed in Table 2. The table suggests that the dependence of K upon n can be neglected as an approximation. Then,

$$K(n, r_0) \equiv K_m = 0.39(\pm 0.08) \quad (22)$$

was used for the calculation of the normalized cell volume, where K_m is the average value of K . It should be noted that those five approximations are not essential to the present theory but unavoidable to calculate the normalized cell volume because the number of

Table 2. The bulk modulus ratio, $K=k_{\text{OH}}/k_{\text{F}}$, and the calculated normalized cell volume.*

Mineral and number	K	V_{cal} ($\text{\AA}^3$)	$V_{\text{cal}} - V_{\text{obs}}$ ($\text{\AA}^3$)
Norbergite 1	0.29 (6)	70.59 (13)	0.05
Chondrodite 2	0.35 (4)	71.89 (7)	0.03
Chondrodite 24	0.39 (4)	72.25 (9)	0.01
Humite 3	0.54 (3)	72.28 (6)	-0.12
Humite 7	0.40 (6)	72.43 (6)	-0.01
Clinohumite 7	0.37 (8)	72.53 (4)	0.01
Clinohumite 10	—	73.05 (2)	0.07
mean	0.39 (8)		

* Estimated standard deviations are given in parentheses and refer to last digit.

available data is poor. It should be also noted that those approximations except eq. (22) are obtained independently of the data on the composition and the normalized cell volume of seven natural humites listed in Table 1.

The volume, V_{cal} , calculated by eqs. (11), (13), (16), (17), (19) and (22) is listed in Table 2. The relation between $V(x, n, r_0)$, x and n is shown in Figs. 1 and 2, where V_{red} listed in Table 1 is also plotted.

The standard deviations of V_{cal} and K , except those of clinohumite 10, were evaluated by

$$(\delta V_{\text{cal}})^2 = \sum_i \left[\left\{ \left(\frac{\partial V_{\text{cal}}}{\partial \xi} \right)_{K_m} + \frac{\partial V_{\text{cal}}}{\partial K_m} \frac{\partial K_m}{\partial \xi} \right\} \delta \xi \right]^2 + \left[\frac{\partial V_{\text{cal}}}{\partial K_m} \delta K_m \right]^2 \quad (23)$$

Fig. 1. The V - $1/n$ diagram of the relation between the normalized cell volume and the anion composition when $\bar{r} = r_0$ ($0.720 \text{ \AA}$). V_{red} are plotted by squares (norbergite, $n=1$), double circles (chondrodite, $n=2$), triangles (humite, $n=3$) and circles (clinohumite, $n=4$). The solid figures indicate end-members.

Fig. 2. The V - x diagram of the relation between the normalized cell volume and anion composition when $\bar{r}=r_0$ ($0.720\text{\AA}$).

and

$$\langle \delta K \rangle^2 = \sum_{\xi} \left[\frac{\partial K}{\partial \xi} \delta \xi \right]^2, \quad (24)$$

where ξ are x , V_F , V_{OH} , A , $\Delta \bar{r}$ and V_{obs} . Since V_F of chondrodite and clinohumite were estimated by eq. (16), their deviations, δV_F , were assumed to be equal to δV_F of humite ($0.04\text{\AA}^3$). δV_{OH} of norbergite was assumed to be $1\text{\AA}^3$ because V_{OH} of norbergite was estimated by extrapolation of eq. (17) which was determined from V_{OH} of chondrodite and clinohumite. δV_{OH} of humite was assumed to be equal to δV_{OH} of chondrodite ($0.02\text{\AA}^3$). δA was assumed to be $10\text{\AA}^2$ because of the following reason: A was determined from the relation of the normalized cell volume and the octahedral cation radius in olivines. And the normalized cell volume of calcium

analogue of chondrodite, $\text{Ca}(\text{OH})_2 \cdot 2\text{Ca}_2\text{SiO}_4$, (Buckle and Taylor, 1958) is $0.8 \pm 1.2 \text{ \AA}^3$ smaller than that of $\gamma\text{-Ca}_2\text{SiO}_4$ which is reported by Smith *et al.* (1965), although the normalized cell volume of hydroxyl-chondrodite is $1.25 \pm 0.02 \text{ \AA}^3$ larger than that of forsterite.

Excepting norbergite 1, the terms of $\delta\xi$ in eq. (23) are numerically negligible if they are compared with that of δK_m . In the case of norbergite 1, the terms of δV_{OH} is larger than that of δK_m . The term of δV_F is one of predominant terms of eq. (24) in six crystals listed in Table 2. In the case of norbergite 1, the term of δV_{OH} is as great as that of δV_F . In the cases of chondrodite 24, humite 7 and clinohumite 7, the term of δA is as great as that of δV_F . It is noted that the errors due to approximation (i) ($V_{\text{OTi}} = V_{\text{OH}}$ and $k_{\text{OTi}} = k_{\text{OH}}$) are not evaluated by eqs. (23) and (24). It is reasonable to consider that these errors are large in clinohumite 10 and humite 3, which contain relatively large amount of Ti. Table 2 suggests that the errors of K and V_{cal} due to approximation (i) are approximately 0.1 and $0.1 \text{ \AA}^3$, respectively.

Discussion

Effects of anion and cation substitutions on the cell volume

The seven natural humites listed in Table 1 have the larger normalized cell volumes than the fluor humites. Jones *et al.* (1969) supposed without numerical evaluations that those minerals contained other cations in addition to Mg (mainly Fe) and therefore have larger cell volumes than the fluor-humites. The validity of their suspicion can be examined by

$$V_{\text{obs}}(\bar{r}) - V_F(r_0) = A \cdot \Delta \bar{r} + \{V_{\text{red}} - V_F(r_0)\}. \quad (25)$$

The first term in the right side expresses the amount of the effect of the replacement of Mg by other cations and the second is that of F by OH and O_{Ti} . The comparison of these values is shown in Table 3. The table shows that the effect of anion substitution on

Table 3. Effects of cation and anion substitutions on the normalized cell volume.*

Mineral and number	$A \cdot Ar$ ($\text{\AA}^3$)	$V_{\text{red}} - V_F$ ($\text{\AA}^3$)
Norbergite 1	0.015 (2)	0.16 (2)
Chondrodite 2	0.048 (5)	0.38 (4)
Chondrodite 24	0.237 (26)	0.58 (5)
Humite 3	-0.037 (4)	0.65 (4)
Humite 7	0.279 (31)	0.38 (5)
Clinohumite 7	0.293 (32)	0.26 (5)
Clinohumite 10	0.037 (4)	0.99 (5)

* Estimated standard deviations are given in parentheses and refer to last digit.

the cell volume is rather greater than that of cation substitution and their supposition is wrong.

Comparison with the linear relation

In the case of the Ti-free humites, the linear relation between the normalized cell volume and average anion radius is expressed by

$$V = (1-x)V_F + xV_{OH}. \quad (26)$$

It is reasonable to consider that this equation can be extended to samples containing small amount of Ti with good approximation, since the radius of the three-coordinated O^{-2} is very close to that of OH (Yamamoto, 1977) and a large error due to approximation (i) ($V_{OTi} = V_{OH}$ and $k_{OTi} = k_{OH}$) has not been found out in the calculation of the normalized cell volume. The relation of eq. (26) in chondrodite is illustrated by a dashed line in Fig. 2. The figure shows that the linear relation is inadequate. On the other hand, eq. (13) agree with eq. (26) when $K \equiv k_{OH}/k_F = V_{OH}/V_F$ or $V_{OH} = V_F$. The inadequacy of the linear relation is caused by the fact that the bulk modulus

ratio, K , differs far from the normalized cell volume ratio $V_{\text{OH}}/V_{\text{F}}$.

Application of the formula

In most crystallographic and chemical analyses of the humites, unit cell parameters and cation proportions were reported but anion proportions were not. Eqs. (7) and (11) provide a method to estimate the three-coordinated anion site composition, since x_3 is determined from Ti-content. It is convenient to this purpose that these equations are rewritten as

$$x_1 = \frac{(1-x_3)V_{\text{OH}}V_{\text{OTi}}(V_{\text{red}}-V_{\text{F}})-x_3V_{\text{F}}V_{\text{OH}}(V_{\text{OTi}}-V_{\text{red}})(k_{\text{OTi}}/k_{\text{F}})}{V_{\text{OH}}V_{\text{OTi}}(V_{\text{red}}-V_{\text{F}})+V_{\text{F}}V_{\text{OTi}}(V_{\text{OH}}-V_{\text{red}})(k_{\text{OH}}/k_{\text{F}})} \quad (27a)$$

$$\cong \frac{V_{\text{OH}}(V_{\text{red}}-V_{\text{F}})}{V_{\text{OH}}(V_{\text{red}}-V_{\text{F}})+V_{\text{F}}(V_{\text{OH}}-V_{\text{red}})K_{\text{m}}} - x_3; \text{ when } x_3 \ll 1. \quad (27b)$$

In the cases of chondrodite, humite and clinohumite which satisfy the conditions, $x_3 < 0.1$ and $\Delta\bar{r} \leq 10^{-3}\text{\AA}$, $K_{\text{m}} = 0.38 \pm 0.02$ is recommended in eq. (27b), where 0.38 is the mean value of K for chondrodite 2, chondrodite 24, humite 7 and clinohumite 7.

Structure features of the humites

It is seen in Table 2 that the dependence of the bulk modulus ratio, K , upon n is weak, although the bulk moduli of OH-humites are approximately four tenths of those of F-humites. This shows that the difference of the bulk moduli between OH-humites and F-humites is caused not only by (OH, F)-M bonding forces but also by the other inter-ionic forces. On the other hand, the replacement of F by OH elongates not only (OH, F)-{Mg, (OH, F), O} distances but also O-{Mg, O} and Mg-{Mg, Si} distances and the cation-occupied octahedra are larger than those expected from simple ionic radius considerations (Yamamoto, 1977). Those evidences suggest that the permanent electric dipole of OH causes the electron clouds of the neighbouring ions, especially O having a high polarizability, slightly broad. After all, the inter-ionic distances and the compres-

sibility of the OH-humites are larger than those of F-humites, and the OH-humites have the larger normalized cell volumes than forsterite. This consideration complements Ribbe, Gibbs and Jones' (1968) explanation of the relation of the normalized cell volume in the humites and forsterite, which can not explain the larger normalized cell volumes of the OH-humites than that of forsterite.

It is possible to regard the difference of the bulk moduli between OH-humites and F-humites as the difference of the bulk moduli between their anion arrays. The anion array of OH-humites is more easily compressed and expanded when compared with F-humites. This consideration explains the fact that many analogues of OH-humites, such as $\text{Mn}(\text{OH})_2 \cdot 3\text{Mn}_2\text{SiO}_4$ ($\bar{r}=0.83\text{\AA}$) and $\text{Ca}(\text{OH})_2 \cdot 2\text{Ca}_2\text{SiO}_4$ ($\bar{r}=1.00\text{\AA}$), have been reported (Moore, 1967; Buckle and Taylor, 1958) but corresponding analogues of F-humites have not, in spite of small difference of ionic radii between OH($1.35\text{\AA}$) and F($1.300\text{\AA}$).

Application of the theoretical model to alkali halides

It is expected that the present theoretical model is applicable to any solid solution system. However, when the crystals in a solid solution system have strong elastic anisotropy, the proportional constants, k_i , in eq. (4) are different from the bulk moduli. The model is applied to $x_1\text{KBr} \cdot x_2\text{KI}$, $x_1\text{NaCl} \cdot x_2\text{NaBr}$ and $x_1\text{KCl} \cdot x_2\text{KBr}$ solid solution systems, where $x_1+x_2=1$, for an example. In these cases, the cell volume differences between end-members are so large that the theory of elasticity for infinitesimal deformation, which has been employed up to now in this paper, is inadequate because the squares and products of strain components are neglected in this theory. The theory of elasticity for finite deformation (Murnaghan, 1951; Birch, 1952), in which no restrictions are imposed on the magnitude of the strain, have to be employed.

In the present case, the formula of a crystal is represented by

$$x_1\text{A}_1 \cdot x_2\text{A}_2, \quad (28)$$

where A_1 and A_2 stand for KBr, KI, NaCl, NaBr and KCl and where

$$x_1 + x_2 = 1. \quad (29)$$

The crystal is composed of small blocks which contain any of the formula units, A_1 or A_2 , and which have the volume, V' . The deformation energy, ϕ_i , of A_i block is given by

$$\phi_i = (9/2)k_i V_i f_i^2, \quad (i=1 \text{ and } 2) \quad (30)$$

where f_i is a finite strain and

$$f_i = (1/2)(V_i^{2/3} - V'^{2/3})/V'^{2/3} \quad (31)$$

and where V_i is the volume of the block in the crystal having the end-composition, A_i , and k_i is the bulk modulus of A_i block at unstressed state. The actual volume, V , of blocks in the crystal having the composition, (28), satisfies the condition that the total strain energy of all blocks is minimum, then

$$\left[\frac{d}{dV'} \sum_{i=1}^2 N x_i \phi_i \right]_{V'=V} = 0, \quad (32)$$

where N is the number of blocks in the crystal. Eqs. (30), (31) and (32) yield

$$V^{2/3} = \left[\sum_{i=1}^2 x_i k_i V_i^{7/3} \right] / \left[\sum_{i=1}^2 x_i k_i V_i^{5/3} \right]. \quad (33)$$

The crystal under consideration is NaCl type, then

$$V = a^3/4, \quad (34)$$

where a is the lattice parameter of the crystal. Therefore, eq. (33) is rewritten as

$$a^2 = \left[\sum_{i=1}^2 x_i k_i a_i^7 \right] / \left[\sum_{i=1}^2 x_i k_i a_i^5 \right] \quad (35)$$

$$= a_1^2 [1 - x_2 \{1 - K(a_2/a_1)^7\}] / [1 - x_2 \{1 - K(a_2/a_1)^5\}] \quad (36)$$

or

Table 4. Calculated and observed cell parameter and bulk modulus ratio and some parameters used for the calculation in alkali halide solid solution system.*

System	x_1	x_2	k_{obs} $\times 10^{11} \text{ dyn/cm}^2$	$a_{\text{obs}}^{\text{d}}$ (Å)	$a_{1\text{r}}$ (Å)	$a_{1\text{r}} - a_{\text{obs}}$ (Å)	a_{cal} (Å)	$a_{\text{cal}} - a_{\text{obs}}$ (Å)	K_{obs}	K_{cal}
$x_1\text{NaCl} \cdot x_2\text{NaBr}$										
	1	0	2.339(12) ^a	5.6402(2)?					0.817 (4)	
	2/3	1/3		5.7614(2)	5.7525(2)	-0.0089	5.7615(4)	0.0001		0.816 (3)
	1/3	2/3		5.8676(2)	5.8649(2)	-0.0027	5.8734(4)	0.0058		0.754 (3)
	0	1	1.911(2) ^b	5.9772(3)?						
$x_1\text{KCl} \cdot x_2\text{KBr}$										
	1	0	1.732(9) ^a	6.2931(3)?					0.822 (4)	
	1/2	1/2		6.4484(3)?	6.4449(3)	-0.0035	6.4496(5)	0.0012		0.809 (5)
	0	1	1.424(1) ^c	6.5966(6)?						
$x_1\text{KBr} \cdot x_2\text{KI}$										
	1	0	1.424(1) ^c	6.5966(6)?					0.774(1)	
	2/3	1/3		6.7624(3)	6.7529(4)	-0.0095	6.7658(4)	0.0034		0.750 (3)
	1/3	2/3		6.9174(3)	6.9092(3)	-0.0082	6.9216(3)	0.0042		0.743 (3)
	0	1	1.102(1) ^c	7.0655(3)?						

References: a; Bartels and Schuele (1965), b; Koliwad, Ghate and Ruoff (1967),

c; Reddy and Ruoff (1965), d; ASTM cards.

* Estimated standard deviations are given in parentheses and refer to the last digit. It is supposed in the evaluation of the deviations that the uncertainty of x_i is less than 0.0001.

$$K \equiv k_2/k_1 = [(1-x_2)(a^2 - a_1^2)a_1^5] / [x(a_2^2 - a^2)a_2^5], \quad (37)$$

where a_i is the lattice parameter of the crystal having the composition, A_i . The lattice parameter, a_{cal} , was calculated by eq. (36) with the observed bulk modulus ratio, K_{obs} . The bulk modulus ratio, K_{cal} , was calculated by eq. (37) with observed lattice parameters. These results are listed in Table 4. The agreements of a_{cal} with a_{obs} are better than 0.1%. The differences between a_{cal} and a_{obs} and between K_{cal} and K_{obs} are, however, larger than the estimated standard deviations, except for (2/3)NaCl·(1/3)NaBr. This is considered to be caused by neglecting the higher order terms than f_i^2 in ϕ_i and the dependence of inter-block forces upon the species of block pairs, as far as the uncertainty of x_i is less than 0.0001.

It is well known that the linear relation accurately holds between the lattice parameter and the composition in the alkali halide solid solution systems. The lattice parameter, a_{lr} , calculated by this relation is also listed in Table 4. The agreement of a_{cal} with a_{obs} is slightly better than that of a_{lr} , except for (1/3)NaCl·(2/3)NaBr.

Conclusions

1. The relation between the composition and the cell volume in the humites and alkali halides were formulated successfully on the basis of the elastic block model. It is expected that this model is applicable to any solid solution systems.

2. The effect of anion substitution on the cell volumes of seven natural humites reported by Jones *et al.* (1969) is greater than that of cation substitution, against their inference.

3. The inadequacy of the linear relation between the anion composition and the cell volume is caused by the fact that $k_{\text{OH}}/k_{\text{F}}$ differs far from $V_{\text{OH}}/V_{\text{F}}$.

4. (OH, F)-O interaction is one of the significant factors to

determine the cell volume and the elastic properties of the humites.

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