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Determination of Variable Atom Parameters in Ionic Crystals by Electrostatic Calculations

TAKEO FUJINO* AND LESTER R. MORSS

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

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An electrostatic method to determine variable atom parameters in ionic crystals with experimentally determined unit cell parameters and space group is proposed. The atom parameters are usually chosen to give the maximum Madelung constant. However, when these atom parameters generate interatomic distances at least one of which is less than a critical distance, which comes from repulsion between atoms, the atom parameters corresponding to that distance are assigned. Applicability was examined for three cases: TiO_2 (rutile), UCl_3, and β-Rb_2GeF_6. Agreement between the atom parameters of this method and of literature was good. Some discussion is presented on the basis of this method. In ionic crystals, the atoms with variable parameters are set first using the geometrical arrangement which is the most stable in an electrostatic sense, and then "real" distances are fixed under the interaction of repulsive forces. © 1987 Academic Press, Inc.

Introduction

In ionic crystals, the largest contribution to the cohesive energy is known to be given by the Madelung energy, which is characterized by the Madelung constant, a geometrical property of the crystal structure. The role of the Madelung constant for understanding various crystal structures has been studied extensively by Hoppe (*1*). He calculated the constants for a variety of binary and ternary halides and also for some oxides, and discussed the Madelung energy of each structure type in combination with the ionic charge quotient, *Q*. He also showed that the chlorine atom parameter in cubic K_2PtCl_6 is a measure of complex nature of $PtCl_6^{2-}$ in the crystal and that it is related functionally to the Madelung constant.

A well known example which shows the usefulness of the Madelung energy is the work by de Boer *et al.* (*2*) where they explained the relative stability of normal and inverse spinels by means of Madelung energy change with order parameter of the two forms although the other theories which invoke *d*-orbital-based crystal field energy (*3, 4*) or pseudo-potential orbital radii (*5*) have appeared subsequently.

Most crystal structures have variable atom parameters. The relation between the Madelung constant and atom parameters was studied many years ago for rhombohedral corundum, Al_2O_3 (*6*), in which the approximation that each aluminum atom is equidistant from six oxygen atoms was made. More recently, Baur (*7*) calculated the Madelung constant of TiO_2 (rutile) as a

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* Present address: Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki, 319-11, Japan.

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function of c/a and an atom parameter, x, and obtained lattice energies of nine rutile-type compounds using Born model calculation in combination with nonelectrostatic Lennard-Jones-type repulsive potentials. Meyer and Hoppe (*8*) took a somewhat different approach. They showed that the variable atom parameter, z, of $NaNbO_2$ (hexagonal, $P6_3/mmc$, $LiNbO_2$ type) was able to be obtained as the point which gives a minimum difference between MAPLE ($NaNbO_2$) and (MAPLE(Na_2O) + MAPLE (Nb_2O_3))/2 on the basis of the additivity of MAPLE, i.e., Madelung Part of Lattice Energy (*1*, *9*).

The variation of the Madelung constant with atom parameter, u, for Y_2O_3 which has a bixbyite-type structure (cubic, space group $Ia3$, T_h^7) has been examined by v. Mertens and Zemann (*10*). In this structure, 8 yttrium atoms, Y1, are in 8(*b*) position with ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), etc., and 24 yttrium atoms, Y2, in 24(*d*) position with (u, 0, $\frac{1}{4}$), etc., and 48 oxygen atoms in 48(*e*) position with (x, y, z), etc. They set the condition that all the Y–O distances were equal and constant (2.2834 Å). This does not hold in the real crystal, but the condition above diminishes the number of variables from four to one; i.e., u. Meanwhile, the atom parameters x, y, and z as well as lattice parameter, a_0, vary as a function of u. According to them, the u value giving the maximum Madelung constant corresponds very well to the observed structure ($u = -0.0328$) (*11*).

It is significant that the results of v. Mertens and Zemann (*10*) could explain the atom parameter without using sophisticated minimization processes in the lattice energy calculations. However, their conditions imposed on the Y–O interatomic distances appear to be too strong, and result in u changing systematically with the lattice parameter.

It is desirable to exploit a simple method which enables us to determine the variable atom parameters in ionic crystals. Actually in some cases, e.g., for highly radioactive specimens, while the crystal system, space group, and lattice parameters can be determined by either X-ray or neutron diffraction analysis, the intensity data collected in the diffraction experiments will not be accurate enough to determine the atom parameters. The aim of the present paper is to establish the possibility of determining the variable atom parameters by simple electrostatic calculations that find the maximum Madelung constant.

Description of the Method

The variable atom parameters will be determined as the quantities which satisfy the following two conditions: (1) At the position of the "true" atom parameter, the Madelung constant as a function of the parameter takes its maximum value. (2) The condition above cannot be attained if it requires that the nearest ion–ion separations in the crystal are less than certain critical values which arise from repulsive interactions between the ions. In this case, the atom parameter is taken as the value which gives the largest Madelung constant under the restriction that the interatomic distances are equal to or larger than the critical lengths which we will propose in the following sections. Observed crystal symmetry and unit cell parameters are of course maintained.

The actual procedure which will be the most common is as follows: One first starts from the reasonably near or "ideal" atom parameter, and calculates the Madelung constants for several varying values of the atom parameter. The parameter value which gives the maximum constant is what we want to determine if the atomic separations are not less than the critical values. Therefore, it is better to calculate the nearest interatomic separations in the crystal for every value of that parameter to check whether the separations are larger than the critical values. If less, one takes the parameter value corresponding to the largest Madelung constant under the condition that the separations are equal to or larger than those critical values. For crystals with two variable parameters, one should construct a two-dimensional matrix of Madelung constants for these parameters, follow the "ridge" in the matrix, and find the point which gives the maximum of the Madelung constant. If the crystal has more than two variable parameters, one constructs several two-dimensional matrices of Madelung constants for pairs of explicitly chosen parameters. In these processes any pair of atoms should have the separation equal to or larger than the respective critical distances.

Calculation of the Madelung Constants

The Madelung constants were calculated using the method of Bertaut (*12, 13*). As the ionic charge distribution, the linear function $f(r) = a(R - r)$ was taken (*14*). The Madelung energy is

$$E(\text{Madelung}) = \frac{288\pi R^2}{VZ} \sum_{\boldsymbol{h}} |F(\boldsymbol{h})|^2 \times \frac{(\alpha \sin \alpha + 2 \cos \alpha - 2)^{10}}{\alpha^{10}} - \frac{26}{35RZ} \sum_{j} (q_j e)^2, \quad (1)$$

where

$$\alpha = 2\pi h R \quad (2)$$

and

$$F(\boldsymbol{h}) = \sum_{j} (q_j e)\exp(2\pi i \boldsymbol{h}\boldsymbol{r}). \quad (3)$$

In these equations, R is half of the shortest interatomic distance, V is the volume of the unit cell, Z is the number of molecules in the unit cell, h is the magnitude of the vector $\boldsymbol{h}(h, k, l)$ in reciprocal space, $\boldsymbol{r}$ is the position vector of the atoms in the crystal, q_j is the charge number of ion j, and e is the electronic charge. The Madelung constant, A, is then expressed by

$$A = -2R \cdot E(\text{Madelung}). \quad (4)$$

Calculations were performed on a FACOM VP-100, and the correctness of the program was checked by comparing with the Madelung constants of Johnson and Templeton (*15*). Agreement was quite good; for example, for TiO_2 (rutile) with their values of $a = 4.5929$, $c = 2.9591$ Å, and $u = 0.3056$, the calculation showed $A = 19.08027$ by summing for h's within the sphere of 4.115 $Å^{-1}$ in reciprocal space, and the value of Johnson and Templeton was 19.0803. Another check was made by doing the calculation for CsCl with different descriptions of this crystal, i.e., cubic, tetragonal, rhombohedral, triclinic, monoclinic, and orthorhombic systems. Each of our values was well in accord with that of Van Gool and Piken (*16*). The Madelung constants are 1.76252 (average of six of our values), 1.7623 (average of the six values of Van Gool and Piken), and 1.76267 (*17*).

Atom Parameter Determination for a Few Ionic Crystals

Applicability of the present method was examined for the following three cases chosen rather arbitrarily.

1. TiO_2 (Rutile)

Titanium dioxide (rutile) crystallizes in the tetragonal system, space group $P4_2/mnm$ (D_{4h}^{14}) with $Z = 2$. In this crystal, 2Ti atoms are in 2(*a*) (0, 0, 0) and ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and 4O in 4(*f*) $(x, x, 0)$, $(\bar{x}, \bar{x}, 0)$, $(\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2})$ and $(x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \frac{1}{2})$.

Abrahams and Bernstein (*18*) made a close examination of the crystal structure by means of X-ray diffraction analysis. They gave $a = 4.59366$, $c = 2.95868$ Å, and $x = 0.3051$ using the isotropic temperature factor refinement, which are in good agreement with the neutron diffraction results, viz. $a = 4.5922$, $c = 2.9590$ Å, and $x = 0.3051$ (*19*). We use here the lattice parameters from the neutron diffraction analysis.

The Madelung constants are given in Table I for several x values, and the variation of the constant is illustrated in Fig. 1. It is seen from the figure that the maximum of the Madelung constant was attained at $x = 0.3020$. The x value accords with the diffraction results though our value is 0.0031 smaller.

As for the critical distances, no systematic efforts to determine them have been exerted yet, but, as will be discussed later, the values may be regarded to be a little smaller than the sum of the crystal radii of Shannon (*20*). This is because the critical distances should reflect the very short range repulsive interactions and the crystal radii are the empirical equilibrium values. We take tentatively in this work $r_A + r_B - 0.1$ Å as the critical distance where r_A and r_B are the crystal radii of Shannon for ions A and B.

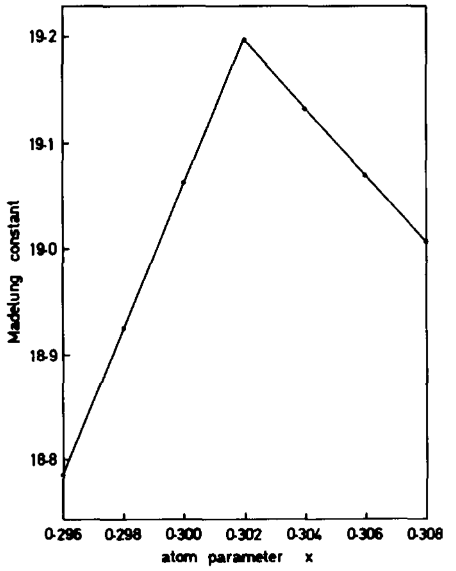

FIG. 1. Variation of Madelung constant with atom parameter x of TiO_2 (rutile).

TABLE I

CHANGE OF MADELUNG CONSTANT, MADELUNG ENERGY, AND HALF THE SHORTEST INTERATOMIC DISTANCE AS A FUNCTION OF ATOM PARAMETER x FOR TiO_2 (RUTILE)

Atom parameter x	Half the shortest interatomic distance R (Å)	Madelung constant	Madelung energy (kcal/mole)
0.296	0.961164	18.78533	−3249.48
0.298	0.967658	18.92392	−3251.49
0.300	0.974153	19.06472	−3253.84
0.302	0.980104	19.19705	−3256.53
0.304	0.975856	19.13156	−3259.55
0.306	0.971632	19.06825	−3262.88
0.308	0.967435	19.00702	−3266.52

The interatomic distances for this compound were calculated for the atom parameter obtained by the electrostatic calculations. Table II shows the distances of Ti–O and O–O. The TiO_6 octahedra in rutile consist of four planar equatorial Ti–O bonds and two apical Ti–O bonds normal to the plane. Our calculations resulted in almost the same apical and equatorial Ti–O distances of 1.961 and 1.960 Å, respectively. On the other hand, the diffraction studies give 1.9800 ~ 1.981 and 1.9845 ~ 1.947 Å. Because the crystal radii for Ti^{4+} ($CN = 6$) and O^{2-} are 0.745 and 1.26 Å (*20*), respectively, the critical distance amounts to 1.905 Å, which is smaller than any values above. Note that our x value and hence the Ti–O distances have been obtained only from the lattice parameters of TiO_2 (rutile). The present electrostatic calculations do not show any effect of axial deformations. As for the reason that the apical Ti–O distance is longer than the equatorial distance by 0.0315 ~ 0.034 Å in the diffraction analyses, Baur and Khan (*21*) claimed the existence of significant (~20%) covalency in rutile. Their results agree with those of Kingsbury (*22*) although he rather attached importance to polarization, but seem to contradict Wackman *et al.* (*23*) and Ladd

TABLE II

INTERATOMIC DISTANCES IN TiO_2 (RUTILE) (Å)

Interatomic distance	Abrahams and Bernstein (*18*)	Sabine and Howard (*19*)	Present work
Ti–O (apical)	1.9800	1.981	1.961
Ti–O (equatorial)	1.9485	1.947	1.960
O–O	2.5363	2.531	2.572
O–O	2.7780	2.778	2.773
O–O	2.9587	2.959	2.959

(*24*). The bond nature of this compound is not unambiguously resolved.

It should be mentioned here that there exists no minimum of Madelung energy in Table I. The energy monotonously decreases from −3249.49 for $x = 0.296$ to −3266.53 kcal/mole for $x = 0.308$. The phenomenon of this type sometimes occurs as a result of Eq. (4). Discussion of this subject will be made in the next section.

2. UCl_3

UCl_3 can be considered basically ionic. X-ray diffraction analysis (*25*) showed that this crystal is hexagonal with lattice parameters $a = 7.443$ and $c = 4.321$ Å. These are in good agreement with the recent refined values of $a = 7.444$ and $c = 4.324$ Å (*26*). The space group is $P6_3/m$ (C_{6h}^2), $Z = 2$, in which 2U are in $2(d) \pm (\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and 6Cl in $6(h) \pm (x, y, \frac{1}{4}; \bar{y}, x - y, \frac{1}{4}; y - x, \bar{x}, \frac{1}{4})$ with $x = 0.3009(4)$ and $y = 0.3858(4)$ by neutron diffraction analysis (*27*). In this crystal, six and three chlorine atoms surround a uranium atom forming a tricapped trigonal prism, the distance between chlorine and uranium atoms being 2.931(3) (6×) and 2.937(3) (3×) Å, respectively (*27*).

TABLE III

MADELUNG CONSTANT OF UCl_3 AS A FUNCTION OF ATOM PARAMETERS x AND y

Parameter x	Parameter y 0.383	0.385	0.387	0.389	0.391
0.296	9.20166				
0.297	9.21323				
0.298	9.22494	9.21710			
0.299	9.23678	9.22865			
0.300	9.22086	9.24034	9.23196		
0.301	9.20322	9.25216	9.24349		
0.302		9.23606	9.25516	9.24625	
0.303		9.21822	9.26696	9.25776	
0.304			9.25067	9.26940	9.25998
0.305			9.23265	9.28188	9.27146
0.306				9.26472	9.28308
0.307				9.24650	9.29484
0.308					9.27819
0.309					9.25979

Table III indicates the change of the Madelung constant as a function of atom parameters x and y. (This is the two-dimensional matrix discussed earlier.) The errors of the constants will be less than 10^{-5} by performing the calculations until $h = 4.258$ Å^{-1}. With the values in the table, the x parameter which gives the maximal Madelung constant can be obtained graphically for each y parameter. An example is shown in Fig. 2 for $y = 0.383$ where the maximum of the Madelung constant, 9.2375, is attained at $x = 0.29905$. Results for the y parameters from 0.383 to 0.391 are listed in Table IV.

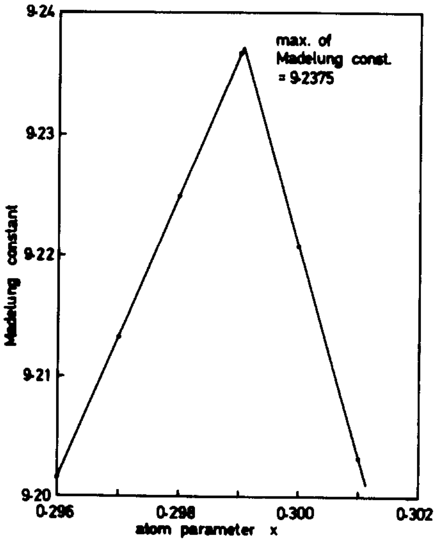

FIG. 2. Variation of Madelung constant with atom parameter x for a fixed parameter $y = 0.383$ of UCl_3.

TABLE IV

ATOM PARAMETER x WHICH GIVES MAXIMAL MADELUNG CONSTANT, MAXIMAL MADELUNG CONSTANT, AND U–Cl DISTANCE FOR SEVERAL y VALUES OF UCl_3

Parameter y	x for maximal Madelung constant[a]	Maximal Madelung constant[a]	U–Cl distance (Å)
0.383	0.29905	9.2375	2.939
0.385	0.30105	9.2529	2.933
0.387	0.30305	9.2677	2.927
0.389	0.30505	9.2818	2.921
0.391	0.30705	9.2955	2.915

[a] Graphically determined.

The relation between the atom parameters x and y is represented in Fig. 3. The figure shows that x increases linearly with y. Another feature from Table IV is that the maximal Madelung constant increases with y in the range $0.383 \leqq y \leqq 0.391$.

The interatomic distances were calculated for pairs of atom parameters x and y. According to the result, the U–Cl distances of nine chlorine atoms around a uranium atom are all the same for each pair of atom parameters which give the maximal Madelung constant, and the distance decreases with increasing y. The calculated values are listed in column 4 of Table IV. The variation is shown in Fig. 3 as a straight line.

We obtain the critical distance of the U–Cl bond in this compound to be 2.92 Å with the crystal radii of U^{3+} and Cl^-, 1.35 and 1.67 Å, respectively. Here, the corrected radius of U^{3+} to nine coordination from six coordination value of Shannon (*20*) was used by taking the difference in radii due to coordination number for trivalent lanthanides, since the increase of coordination number causes a significant increase in crystal radii, especially for cations.

From the above results, the conditions of this paper will be satisfied (first, at least for U–Cl distances) if we choose the x and y parameters corresponding to the U–Cl distance of 2.92 Å in Fig. 3. The values obtained are $x = 0.3054$ and $y = 0.3894$. The Madelung constant, Madelung energy, and half of the shortest interatomic distance of this compound for the above pair of atom parameters are 9.28396, −1057.16 kcal/mole, and 1.460115 Å, respectively. The Cl–Cl distances of the crystal are 3.315(2×), 3.410(2×), and 3.411(4×) Å, which are all larger than the critical distance (3.24 Å) of Cl–Cl bond. The x and y parameters obtained by the present electrostatic calculations are in good agreement with the values reported, although slightly larger. The differences in x and y from Taylor and Wilson (*27*) are 0.0045 and 0.0036, respectively, and from Schleid *et al.* (*26*) 0.0038 and 0.0028, respectively.

3. *β-Rb_2GeF_6*

The high-temperature form of rubidium fluorogermanate, β-Rb_2GeF_6, is hexagonal, with $a = 5.94$ and $c = 9.63$ Å (*28*); the space group is $P6_3mc$ (C_{6v}^4), and there are two formula units ($Z = 2$) per unit cell. The atom parameters are reported to be

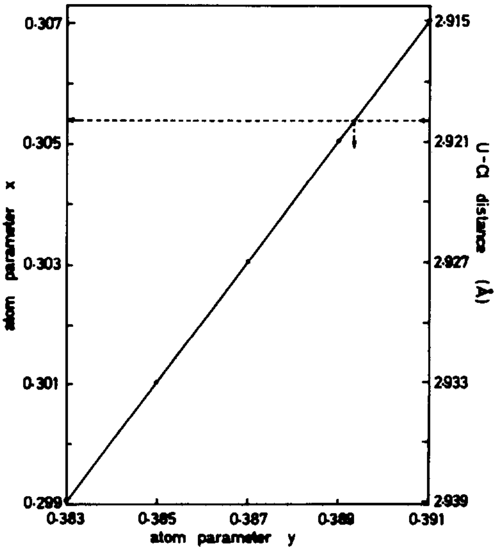

FIG. 3. Variation of atom parameter x, and U–Cl distance with atom parameter y of UCl_3.

2Rb1 in 2(*b*):	$\frac{1}{3}, \frac{2}{3}, u(\text{Rb1}); \frac{2}{3}, \frac{1}{3}, u(\text{Rb1}) + \frac{1}{2}$ with $u(\text{Rb1}) = 0.89$
2Rb2 in 2(*a*):	$0, 0, u(\text{Rb2}); 0, 0, u(\text{Rb2}) + \frac{1}{2}$ with $u(\text{Rb2}) = 0.61$
2Ge in 2(*b*):	with $u(\text{Ge}) = 0.25$
6F1 in 6(*c*):	$u(\text{F1}), \bar{u}(\text{F1}), v(\text{F1}); u(\text{F1}), 2u(\text{F1}), v(\text{F1}); 2\bar{u}(\text{F1}), \bar{u}(\text{F1}), v(\text{F1}); \bar{u}(\text{F1}), u(\text{F1}), v(\text{F1}) + \frac{1}{2}; \bar{u}(\text{F1}), 2\bar{u}(\text{F1}), v(\text{F1}) + \frac{1}{2}; 2u(\text{F1}), u(\text{F1}), v(\text{F1}) + \frac{1}{2}$ with $u(\text{F1}) = 0.18$ and $v(\text{F1}) = 0.35$
6F2 in 6(*c*):	with $u(\text{F2}) = 0.49$, $v(\text{F2}) = 0.15$

Figure 4 shows a perspective view of this crystal structure. As seen from the figure, each germanium atom is coordinated by six fluorine atoms which form an octahedron, and each rubidium atom has 12 nearest-neighbor fluorine atoms. There are seven variable atom parameters in this structure, i.e., $u(\text{Rb1})$, $u(\text{Rb2})$, $u(\text{Ge})$, $u(\text{F1})$, $v(\text{F1})$, $u(\text{F2})$, and $v(\text{F2})$, but all the atoms have the variable parameters along the c axis. Therefore, one of these parameters can be arbitrarily chosen (*29*). We take $u(\text{Ge}) = 0.25$ in order to be consistent with the literature values (*28*).

An atom parameter pair of $u(\text{F1})$ and $v(\text{F1})$, and that of $u(\text{F2})$ and $v(\text{F2})$ were chosen explicitly. First, the Madelung constant was calculated with the reported values of parameters (*28*). Calculations were then carried out by changing the parameters of the $u(\text{F1})$ and $v(\text{F1})$ pair, which revealed that if the atom parameters are taken to yield the maximal Madelung constant, the Ge–F1 (3×) distances are equal to the Ge–F2 (3×) distances which are a function of $u(\text{F2})$ and $v(\text{F2})$. Since there is only one $v(\text{F1})$ parameter value which makes the three Ge–F1 distances equal to the Ge–F2 distances for a given value of $u(\text{F1})$ parameter, the empirical relation above was used to reduce the two variables. That is to say, $v(\text{F1})$ and $v(\text{F2})$ were determined as a function of $u(\text{F1})$ and $u(\text{F2})$, respectively.

Table V represents the Madelung constants for several pairs of $u(\text{F1})$ and $u(\text{F2})$ parameters for $L = 1.88$ Å where L stands for the Ge–F distance. As in the case of UCl_3, one can obtain the $u(\text{F2})$ value which gives the maximal Madelung constant for each of the $u(\text{F1})$ values. This $u(\text{F2})$ and the maximal Madelung constant graphically determined are shown on the lower two lines of the table. According to the graphical

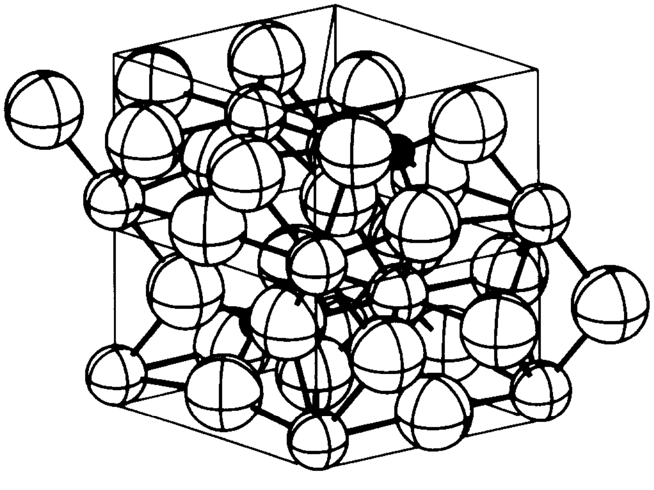

FIG. 4. Perspective view of the hexagonal cell of β-Rb_2GeF_6. Smallest spheres, Ge; middle-sized spheres, Rb; largest spheres, F.

TABLE V

MADELUNG CONSTANT OF Rb_2GeF_6 AS A FUNCTION OF PARAMETERS u(F1) AND u(F2) FOR L = 1.88 Å[a]

Parameter u(F2)	Parameter u(F1) 0.1645	0.1685	0.1725	0.1765
0.458	16.17559	16.17810		
0.462	16.18405	16.18913	16.18296	16.16752
0.466	16.18634	16.19407	16.19043	16.17713
0.470	16.18252	16.19316	16.19220	16.18125
0.474	16.17273	16.18650	16.18845	16.18007
0.478			16.17912	16.17354
u(F2) which gives maximal Madelung constant[b]	0.4656	0.4674	0.4694	0.4713
Maximal Madelung constant[b]	16.1865	16.1945	16.1924	16.1816

[a] Rubidium parameters are u(Rb1) = 0.89 and u(Rb2) = 0.61. L is the Ge–F distance.

[b] Graphically determined.

analysis of the results, the maximum of the maximal Madelung constants which should produce a continuous ridge in this two-dimensional map is located at u(F1) = 0.1698 which results in u(F2) = 0.4681, v(F1) = 0.3371, and v(F2) = 0.1182. The corresponding Madelung constant is 16.1959.

If we take as the critical distance the 0.1 Å smaller value than the crystal radius sum, the critical distances for Rb–F, Ge–F, and F–F are 2.95, 1.76, and 2.28 Å, respectively, since the crystal radii of Rb^+ (CN = 12), Ge^{4+} (CN = 6), and F^- are 1.86, 0.67, and 1.19 Å, respectively (*20*). On calculating the interatomic distances with the above atom parameters and with the literature rubidium parameters, i.e., u(Rb1) = 0.89 and u(Rb2) = 0.61, it was found that three Rb1–F2 and three Rb2–F1 distances were 2.598 and 2.799 Å, respectively. These separations are less than the critical distance of Rb–F (2.95 Å) by 0.352 and 0.151 Å. The rubidium parameters which give 2.95 Å were u(Rb1) = 0.8478 and u(Rb2) = 0.5903. Three remaining Rb2–F1 distances were 2.999 Å with these parameter values. The Madelung constant was 16.15796. This constant is smaller than the former one, which means that the rubidium parameters of 0.8478 and 0.5903 are those which bring about the maximum Madelung constant in agreement with the condition 2.

The same procedure was carried out for L = 1.92 Å. The result is shown in Table VI. The parameter values obtained were u(F1) = 0.1652, v(F1) = 0.3365, u(F2) = 0.4691, and v(F2) = 0.1132. The Madelung constant was 16.2190, which is larger than that for L = 1.88 Å. Therefore, the crystal can be regarded as more stable with the Ge–F distance of 1.92 Å in an electrostatic sense. However, calculation shows that it is impossible to have all Rb–F distances equal or larger than 2.95 Å with L = 1.92 Å. If we put u(Rb1) = 0.8434 and u(Rb2) = 0.5861, the three Rb1–F2 and three Rb2–F1 distances increase to 2.95 Å, but the remaining three Rb2–F1 distances decrease to 2.944 Å which is less than 2.95 Å. Figure 5 shows the change of the remaining Rb2–F1 distance with L. It is seen from the figure that 2.95 Å is attained at L = 1.916 Å. The relation between u(F1) and L is indicated in Fig. 6, and that between u(F2) and L in Fig. 7. By graphical interpolation, the two parameters u(F1) and u(F2) which correspond to L = 1.916 Å are determined to be 0.1657 and 0.4961, respectively. The parameters for β-Rb_2GeF_6 are finally u(Rb1)

TABLE VI

MADELUNG CONSTANT OF Rb_2GeF_6 AS A FUNCTION OF PARAMETERS u(F1) AND u(F2) FOR L = 1.92 Å[a]

Parameter u(F2)	Parameter u(F1) 0.1605	0.1645	0.1685	0.1725
0.458	16.19940			
0.462	16.20920	16.21094	16.20241	
0.466	16.21289	16.21734	16.21123	16.19595
0.470	16.21066	16.21803	16.21450	16.20149
0.474	16.20296	16.21348	16.21275	16.20225
0.478		16.20341	16.20571	16.19796
0.482				16.18860
u(F2) which gives maximal Madelung constant[b]	0.4666	0.4684	0.4708	0.4727
Maximal Madelung constant[b]	16.2130	16.2186	16.2146	16.2025

[a] Rubidium parameters are u(Rb1) = 0.89 and u(Rb2) = 0.61. L is the Ge–F distance.

[b] Graphically determined.

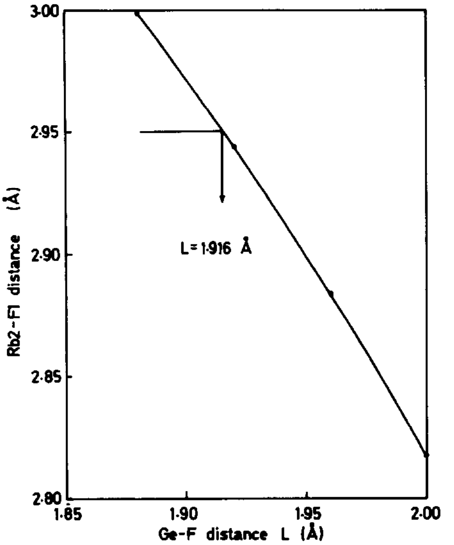

FIG. 5. Variation of shorter Rb2–F1 distance with Ge–F distance of β-Rb_2GeF_6.

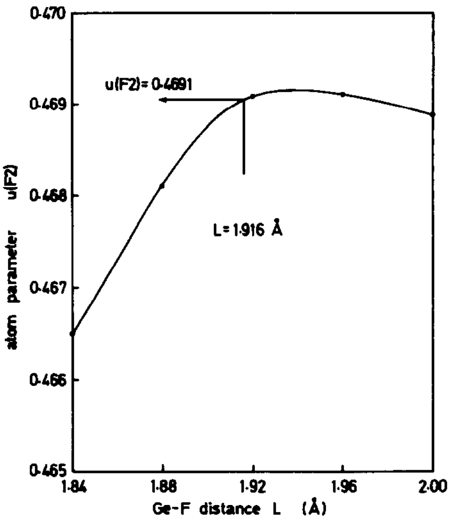

FIG. 7. Relation between atom parameter u(F2) and Ge–F distance for β-Rb_2GeF_6.

= 0.8440, u(Rb2) = 0.5867, u(F1) = 0.1657, v(F1) = 0.3367, u(F2) = 0.4691, and v(F2) = 0.1138 together with one explicit parameter of u(Ge) = 0.25. These values compare well with literature values (*28*). The Madelung constant and the Madelung energy for these parameters are 16.17170 and −2806.59 kcal/mole, respectively. Interatomic distances are as follows: Rb1–F2 = 2.950 (3×) and 3.007 (3×), Rb1–F1 = 2.971 (6×), Rb2–F1 = 2.950 (6×), Rb2–F2 = 2.998 (6×), Ge–F1 = 1.916 (3×), Ge–F2 = 1.916 (3×), F1–F1 (shortest) = 2.953 (2×), F1–F2 (shortest) = 2.669 (2×), and F2–F2 (shortest) = 2.419 (2×) Å.

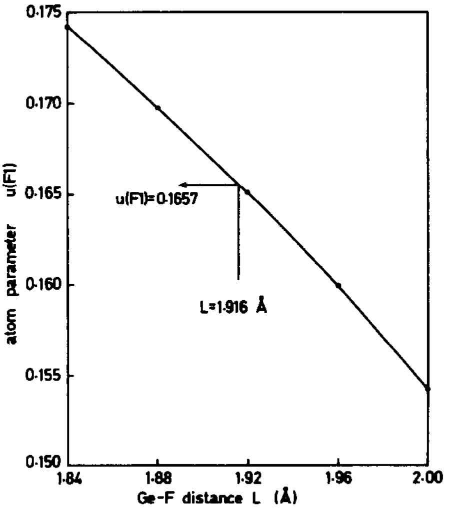

FIG. 6. Relation between atom parameter u(F1) and Ge–F distance for β-Rb_2GeF_6.

Discussion

For the present aim of determining variable atom parameters, we only need to pay attention to the energy components, which vary significantly with the structure-dependent factors, in the cohesive energy of the crystal. This implies that we are not concerned with determination of the precise cohesive energies of crystals. Such factors can be characterized by the lattice sums $\Sigma 1/R^n$ where the summation is to be taken for the whole atomic distances in the crystal. The related energy components other than the Madelung energy are the repulsive and van der Waals energies.

The repulsive energy has mostly been assumed to vary exponentially with the distance of two closed-shell ions in keeping with quantum-mechanical results (*17, 30*). However, the inverse power form of Born and Landé (*31*) will be used for ease of comparison. In this context, the repulsive contribution to the cohesive energies is expressed as

$$E(\text{repulsive}) = \frac{B}{R^n} \quad (5)$$

where the parameters B and n can be determined directly for each crystal from the equation of state and its volume derivative.

It is known in general that the repulsive contribution is 10 ~ 15% of the total cohesive energy (*32*). Because the cohesive energy is given by

$$E(\text{cohesive}) = \frac{NAe^2}{R_0}\left(1 - \frac{1}{n}\right) \quad (6)$$

at equilibrium distance provided that the other smaller energy terms than the Madelung and repulsive energies are neglected, the inverse power figure n is 9 ~ 10 from the equation above, where N is the number of ion pairs and R_0 is the equilibrium distance. The exponent n of the repulsive interaction is so much larger than $n = 1$ for Coulombic interaction that it is not unrealistic to regard the repulsive forces between ions or atoms as very short ranged. That is to say, for our present purpose, no great problems will arise if the approximation that the repulsive interactions are only between nearest-neighbor atoms is taken. In that case, we can consider that the interactions are not primarily affected by the structure of crystals and that they are zero, though the last approximation may be somewhat crude, if the atom–atom separations are larger than some critical values.

Nieuwpoort and Blasse (*33*) have shown that such critical distances could be estimated to be the sum of the *atomic* radius of a metal and the *ionic* radius of an anion, which are about 0.8 Å larger than the crystal equilibrium distances. Our potentials for the repulsive interactions are ∞ inside our critical distances and zero over these. It is possible to take some constant values instead of zero, but this does not change the result since the effect is only to add some constant energy to the cohesive energies for any variable atom parameters.

The van der Waals energy is composed of the dipole–dipole and dipole–quadrupole interactions, which can be written as the sum of the two-body energies (*17*) as

$$E(\text{van der Waals}) = -\frac{C}{R^6} - \frac{D}{R^8} \quad (7)$$

where the coefficients C and D are linear combinations of the van der Waals coefficients for interactions of the various ion pairs weighted by appropriate lattice sums. Again, the van der Waals energies are characterized by far more short-ranged interactions than the Coulombic energies. Their contribution to the cohesive energies is small, of the order of several percent, unless the component ions show large polarizabilities. Bertaut (*34*) has presented a straightforward method to calculate the van der Waals energy of crystals, and has predicted the atom parameter difference between the neutron and X-ray diffraction results for TiO_2 (rutile) to be 0.0123. However, it was not confirmed by Sabine and Howard (*19*) in their neutron diffraction study. It seems that the effect of the van der Waals energies on crystals is still in a state of flux, and we did not calculate these energies in this paper.

It is an important fact that there exists no minimum in the Madelung *energies* of Table I although it has a maximum in the Madelung *constants*. This is because R may change with atom parameters. As shown in Eq. (4), the Madelung energy is given by A divided by $-2R$. We recall that the Madelung constant is a strictly geometrical factor of the structure of ionic crystals without dimension. This means that the Madelung constant indicates how negatively large the Madelung energy is for a given R. The facts that the Madelung constants show maxima and reflect the experimental atom parameters while the Madelung energies do not can be considered to represent that the variable atom parameters are set first as the geometrical positions which give the most negative Madelung energies and then "real" atomic separations are fixed under the circumstances of repulsive interactions. Due to Eq. (4), crystals will take R values as small as possible for a given Madelung constant, but this condition is subordinate to that of maximum Madelung constant.

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