Mem. SR Center Ritsumeikan Univ. No. 27, 19-23 (2025)

The Relation of Electrostatic Potentials and the F 1s XPS Chemical Shifts of Some Fluorides

Kiyotaka Asakura and Daisuke Shibata
SR Center, Ritsumeikan University, Nojihigashi 1-1-1, Kusatsu 525-8577, Japan

The XPS binding energies of F 1s in alkaline and alkaline earth metal fluorides are simply related to the bond distances between the Fluorine and the counter cations. In this work we find the linear relation between the reciprocal bond distance and the electrostatic potential at F created by the other ions V_{int}(F). $V_{int}(\mathrm{F}) = \frac{M_{anion}e}{4\pi\epsilon_0 r_{FC}}$ where $M_{anion} = 1.77$. This linear relationship is the origin of the relation between the binding energy and the bond distance. Madelung constant for LaF$_3$, AlF$_3$ and BeF$_2$ are reported.

1. Introduction

The energy of an X-ray absorption edge is closely tied to the valence state of the central atom; a higher edge energy typically indicates a higher valence state. Fluorine, being the most electronegative halogen, readily forms F$^-$. In the previous research [1], D. Shibata observed edge energy shifts in the F K-edge XAS of various fluorides, even among those with the same formal charge of -1. These edge shifts spanned a range of 5 eV. Notably, for fluorides of alkaline metals, alkaline earth metals, AlF$_3$, and LaF$_3$—where the cations have no extra valence electrons or possess a closed-shell electronic structure (ns^{0}np^0(n-1)d^0)—the position of the absorption edge was inversely proportional to the bond distance between the cation and the fluorine ion.

The edge energy is related to the chemical shifts of XPS (X-ray photoelectron spectroscopy) peaks. Siegbahn et al. provided the following equation for chemical shift ΔE of the XPS peak in free molecule [2].

$$\Delta E = kq_F + \frac{\sum e^2 q_c}{r_{FC}} + l, \tag{1}$$

where q_F, q_c are the formal charges of F and counter cations, respectively. The r_{FC} is the bond distance between F and the counter cation. k and l are constants specific to the element and local environment. If they are independent of the coordination number and the charge of surrounding cations, the peak shift is proportional to the bond distance. However, the eq. (1) involves the q_c and depends on the coordination number through the summation. In the ionic crystal, the long-range Coulomb interaction takes place. The eq. (1) should be modified as

$$\Delta E = kq_F + \sum_{i=C,F} \frac{e^2 q_i}{r_{Fi}} + l, \tag{2}$$

where the sum is taken over all cations and anions in crystal.

If the (2) is rewritten as

$$\Delta E = kq_F + \frac{M_{anion} e^2}{r_{FC}} + l, \tag{3}$$

energy shift would be proportional to $1/r_{FC}$. The question is whether M_{anion} is constant independent of the crystal structures. Compared to eq. (3) and eq. (2), the calculation of M_{anion} is similar to the calculation of the Madelung constant, M_c.

$$U_{le} = \sum_{i,j} \frac{q_F q_C e^2}{2r_{ij}} = \frac{-NM_C e^2}{r_{FC}} = -NM' \frac{q_C(q_C+1)e^2}{2r_{FC}}, \tag{4}$$

where U_{le} is a lattice energy of ionic crystal. The M_c of NaF(rocksalt), CaF$_2$(fluorite) and MgF$_2$(rutile) are 1.748, 5.0388 and 4.816, respectively [3]. M' is reduced Madelung potential and the values are in the range of 1.6 to 1.77 for many crystal structures [4]. When the U$_{le}$ is expressed by the potential energy of F$^-$ and Cation, $V_{int}(\mathrm{F}) = \frac{M_{anion}e}{r_{FC}}$ and $V_{int}(\mathrm{Ca}) = \frac{M_{cation}e}{r_{FC}}$

$$\begin{aligned} U_{le} &= \frac{1}{2}\left(-\sum_{anion} V_{int}(\mathrm{F})e - \sum_{cation} V_{int}(\mathrm{Ca})q_c e\right) \\ &= \frac{1}{2}\left(-\sum_{anion} \frac{M_{anion}e^2}{r_{FC}} - \sum_{cation} \frac{M_{cation}q_c e^2}{r_{FC}}\right) \\ &= -\frac{1}{2}\left(\sum_{anion} M_{anion} + \sum_{cation} M_{cation}\, q_c\right)\frac{e^2}{r_{FC}} \end{aligned} \tag{5}$$

$$\therefore NM_c = \frac{1}{2}\left(\sum_{anion} M_{anion} + \sum_{cation} M_{cation}\, q_c\right) \tag{6}$$

Or

$$NM' \frac{q_c(q_c+1)}{2} = \frac{1}{2}\left(\sum_{anion} M_{anion} + \sum_{cation} M_{cation}\, q_c\right) \tag{6'}$$

where N is a number of ion pairs (Cation-F).

If the cation is monovalent ($q_c = 1$), $M_{anion} = M_{cation}$ so that $M_{anion} = M_c = M'$. In the case of $q_c \neq 1$

$$M' \frac{q_c(q_c+1)}{2} = \frac{1}{2}(M_{anion}q_c + M_{cation}q_c)$$

If $M' = M_{anion} = M_{cation}/q_c$, $M' = M_{anion}$ would be correct. Since M' is almost constant (1.6 -1.77), M_{anion} can be constant. In this paper we calculate $V_{int}(\mathrm{F}) = \frac{M_{anion}e}{r_{FC}}$ in a similar way to the Madelung potential calculation. We have found that the $V_{int}(\mathrm{F})$ is proportional to $1/r_{FC}$ and M_{anion} is constant and equal to 1.77.

2. Theory and Experimental

2.1 Theory

In the Madelung potential calculation, there are two ways because of the slow convergence of the direct calculation of Coulombic potential in real space. One is the Ewald method, [5, 6] and the other approach is the k-space calculation.[7] In this paper, the latter approach is selected and is explained briefly according to the literature.[7]

In an ionic crystal lattice, the ionic charge has periodicity. The charge density, $\rho(\boldsymbol{r})$, can be expressed as,

$$\rho(\boldsymbol{r}) = \sum_j q_j \sigma(\boldsymbol{r} - \boldsymbol{r}_j), \tag{7}$$

where

$$\int_0^R \sigma(r)dr = 1. \tag{8}$$

All charge of the ion is located inside the radius,R. Note that the σ ave the spherical symmetry because the ions have the closed-shell. Since $\boldsymbol{r_j}$ is on the crystal lattice point, $\rho(\boldsymbol{r})$ has periodicity and can be expanded in the Fourier series.

$$\rho(\boldsymbol{r}) = \sum_j A_h \exp(-2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}), \tag{9}$$

$\boldsymbol{h}$ is a reciprocal unit vector.

The coefficient $A_{\boldsymbol{h}}$ is expressed in the inverse Fourier transformation.

$$\begin{aligned} A_{\boldsymbol{h}} &= \frac{1}{v}\int_{\mathrm{C}} \rho(\mathbf{r}) \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \mathrm{d}^3\boldsymbol{r} \\ &= \frac{1}{v}\int \sum_j q_j \sigma(\boldsymbol{r} - \boldsymbol{r}_j) \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \mathrm{d}^3\boldsymbol{r} \\ &= \frac{1}{v}\sum_j q_j \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}_j) \int_{\mathrm{C}} \sigma(\boldsymbol{r}) \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \mathrm{d}^3\boldsymbol{r} \\ &= \frac{1}{v} F(\boldsymbol{h})\phi(\boldsymbol{h}) = A_h \end{aligned} \tag{10}$$

Since the crystal is electrically neutral,

$$\begin{aligned} A_0 &= \frac{1}{v}\int \sum_j q_j \sigma(\boldsymbol{r} - \boldsymbol{r}_j)\, \mathrm{d}^3\boldsymbol{r} \\ &= \frac{1}{v}\sum_j q_j \int \sigma(\boldsymbol{r} - \boldsymbol{r}_j) \mathrm{d}^3\boldsymbol{r} = 0 \end{aligned}$$

$$F(\boldsymbol{h}) = \sum_{j \in C} q_j \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}_j) \tag{11}$$

$F(\boldsymbol{h})$ is the structure factor of the point charges.

$$\phi(\boldsymbol{h}) = \int_{\mathrm{C}} \sigma(\boldsymbol{r}) \exp(2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r} \tag{12}$$

Consequently, eq. (9) and eq. (10) provide

$$\rho(\boldsymbol{r}) = \tfrac{1}{v}\textstyle\sum_{\boldsymbol{h} \neq 0} F(\boldsymbol{h})\phi(\boldsymbol{h}) \exp(-2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \tag{13}$$

Similarly, Coulombic potential $V(\boldsymbol{r})$ can be expanded in the Fourier series,

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{h}} B_{\boldsymbol{h}} \exp(-2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \tag{14}$$

Furthermore, Poisson's equation links potential to the charge density.

$$\nabla^2 V(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r}) \tag{15}$$

Substituting the (14) and (15) into (13), $B_{\boldsymbol{h}}$ is expressed simply as

$$B_{\boldsymbol{h}} = \frac{1}{\pi v} \frac{F(\boldsymbol{h})\phi(\boldsymbol{h})}{|\boldsymbol{h}|^2} \;;\; B_0 = 0 \tag{16}$$

Finally, we have total potential at position $\boldsymbol{r}$, $V_{tot}(\boldsymbol{r})$, in the Fourier Series.

$$V_{tot}(\boldsymbol{r}) = \frac{1}{\pi v}\sum_{\boldsymbol{h} \neq \boldsymbol{0}} \frac{F(\boldsymbol{h})\phi(\boldsymbol{h})}{|\boldsymbol{h}|^2} \exp(-2\pi i\, \boldsymbol{h} \cdot \boldsymbol{r}) \tag{17}$$

Then the electrostatic potential of one ion site $V_{int}(\boldsymbol{r_j})$ created by the other ions can be obtained by removal of the self energy $V_s(\mathbf{0})$

$$V_s(\mathbf{0}) = \frac{q_j}{\pi}\int \frac{\phi(\boldsymbol{h})d^3\boldsymbol{h}}{|\boldsymbol{h}|^2} \tag{18}$$

$$V_{int}(\boldsymbol{r_j}) = \frac{1}{\pi v}\sum_{\boldsymbol{h}\neq\mathbf{0}} \frac{F(\boldsymbol{h})\phi(\boldsymbol{h})}{|\boldsymbol{h}|^2}\exp(-2\pi i\,\boldsymbol{h}\cdot\boldsymbol{r_j}) - \frac{q_j}{\pi}\int \frac{\phi(\boldsymbol{h})}{|\boldsymbol{h}|^2}d^3\boldsymbol{h} \tag{19}$$

Madelung energy per unit cell can be obtained as

$$W_{Mad} = \frac{1}{2}\sum_i q_i e V_{int}(\boldsymbol{r}_i) \tag{20}$$

The program, written in Python, can be found in Supporting Information. The XPS spectra were measured with Quantas (ULVAC-PHI Co) installed at SA-1. The monochromatized Al Kα (1486.7 eV) was focused on the sample. The F 1s peak position was calibrated using the C1s = 284.7 eV.

3. Result

3.1 The dependence of $V_{int}(\boldsymbol{r}_i)$ on the R

Given that $V_{int}(\boldsymbol{r}_i)$ includes $\phi(\boldsymbol{h}) = \int_C \sigma(\boldsymbol{r})\exp(2\pi i\,\boldsymbol{h}\cdot\boldsymbol{r})\,d^3\boldsymbol{r}$, where $\sigma(\boldsymbol{r})$ is a charge density distribution function, calculating $V_{int}(\boldsymbol{r}_i)$ consequently requires knowledge of $\sigma(\boldsymbol{r})$, charge distribution. This implies the necessity of quantum chemical calculations to obtain accurate charge distributions. However, F^- and other ions in this case, have a closed-shell and $\sigma(\boldsymbol{r})$ has a spherical shape. According to the Gauss theory, electric field coming from the sphere with radius *R* is independent of the charge distribution inside the radius *R*. Thus, we take an appropriate *R* in which all charges are located. First, the $V_{int}(\boldsymbol{r}_i)$ and M_c of NaF were calculated with the different *R*. Figure 1 shows the M_c (Madelung constant) of NaF as a function of $|\boldsymbol{h}|$ (Reciprocal lattice) with different *R* in the range of 0.231 Å (one-tenth of bond distance) to 4.62Å (equal to twice as large as the bond distance). When $R = 0.231$Å, the M_c oscillates largely and is converged to 1.747 with $|\boldsymbol{h}| > 20$. When we select the larger *R*, we can obtain reasonable M_c with less oscillation. In $R > r_{FC}$ the M_c becomes smaller than 1.747. At $R = 2\,r_{FC}$, $M_c = 0.35$. We have selected $R = r_{FC}$, where two spheres contact each other.

3.2 Crystal structure

Table 1 shows the samples and their crystal structures examined in this work. Most of them are cubic or tetragonal. LaF_3 and AlF_3 are hexagonal and rhombohedral, respectively and ions are located at several different sites and hence different r_{FC}. Consequently, we used average r_{FC} and $V_{int}(\boldsymbol{r}_i)$ for LaF_3 and AlF_3. The calculated $V_{int}(\boldsymbol{r}_i)$ and M_c are listed in Table 1. M_c are well corresponding to the values in literature.[4] In Table 1 V_{int}(F) and V_{int}(Ca) mean the potentials at the F and Cation(not Calcium) sites, respectively. Note that to gives the V_{int}(F) in MKSA unit, we multiplied $14.4 = e/4\pi\epsilon_0$. In monovalent alkaline cations, the $V_{int}(\text{F}) = V_{int}(\text{Ca})$ as expected while for divalent alkaline earth cations except BeF_2, V_{int}(Ca) is a little less than $V_{int}(\text{F}) \times 2$. BeF_2 is much smaller V_{int}(Ca) than the $V_{int}(\text{F}) \times 2$ as discussed later. Trivalent species such as La and Al have a smaller V_{int}(Ca) than the $V_{int}(\text{F}) \times 3$. Thus, our first guess of $M' = M_{anion} = M_{cation}/q_c$ would be wrong.

Figure 2 shows the V_{int}(F) dependence on the $1/r_{FC}$. We have found that $V_{int}(F)$ increases with $1/r_{FC}$. The data are fitted with a linear line where the slope and intercept are 31.40 V Å and -2.41 V, respectively. When we look at the data more closely, we may find the points except BeF_2 are on the linear line. If we plot the data without BeF_2, they appear just on a linear line. If we fit all data, we get the *R*-factor = 0.08, which is defined as $\sqrt{\left(\frac{\Sigma(y_{cal}-y_{fit})^2}{\Sigma y_{fif}{}^2}\right)}$ while we can get better *R*-factor = 0.01 using the data without the BeF_2 point. The fitting result is $27.01/r_{FC} - 0.66$. The intercept becomes small. If the intercept is set to 0, we can get the 25.56/r with not so bad *R* factor (0.02) as shown in the green dotted line of Figure 2. Interestingly, $25.56 = 1.77 * 14.4(= e\ /4\pi\epsilon_0)$ or $M_{anion} = 1.77$ is similar to the value of M_c of NaCl type(1.757).

3.3 The XPS chemical shifts and $V_{int}(F)$

Figure 3 shows the relation between F 1s XPS chemical shifts and V_{int}(F). There is a well corresponding relation between V_{int}(F) and the chemical shift of XPS. According to the eq. (3) $\Delta E(eV) = e\,V_{int}(\text{F})(\text{Volt})$. We draw the linear line with slope 1 as shown in Figure 3. The intercept is 673.6 ± 1.8 eV, which might correspond to the 1s electron binding energy of isolated F^-.

4. Discussion

The calculation of V_{int}(F) depends on the charge density of σ where R is an important parameter. When $R = r_{FC}/10$ is selected, the convergence of the series is slow and requires the large $|\boldsymbol{h}| > 20$. When we select $R = r_{FC}/2$ and $R = r_{FC}$, the values are rapidly converged with $|\boldsymbol{h}|$ = 9 and 2, respectively to give Mc =1.747. At $R = r_{FC} \times 1.1$, it gives the smaller Madelung constant and V_{int}(F) in NaF as 1.67, $V_{int}(\text{F}) = 10.37$ V, respectively. At $R = r_{FC} \times 2$, the Mc becomes 0.35 abnormally smaller. R must not be more than r_{FC}. The $R = r_{FC}$ is already phycially meaningless because the homogenously distributed charge spheres overlap though the convergence is faster. In this sense we select $R = r_{FC}/2$ where the two spheres are touching but not overlapping. Only BeF$_2$ does not appear on the line. Figure 4 shows the R dependence of the V_{int}(F). We calculate the V_{int}(F) up to $|\boldsymbol{h}| = 50$ where the V_{int}(F) is converged in the case of NaF even in $R = r_{FC}/10$. As shown in Figure 4, the M_C continuously decreases and it takes a plateau at $R = r_{FC}/2$, where the M_C gradually decreases. At $R > r_{FC}$, the M_C starts to decrease largely. At $R = r_{FC}$, V_{int} (F) = 16.6 V in BeF$_2$, which appears on the linear line as shown in Figure 2. Although the BeF$_2$ behaves in a different way from the others, all other species follow the common features of V_{int} (F) for the r_{FC},

$$V_{int} = \frac{M_{anion} e}{4\pi\epsilon_o r_{FC}} \tag{21}$$

where $M_{anion} = 1.77$. We conclude that eq. (21) should be valid for F$^-$ bound to the closed shell cations or the cations with ns^{0}np^0(n-1)d^0 electronic configurations.

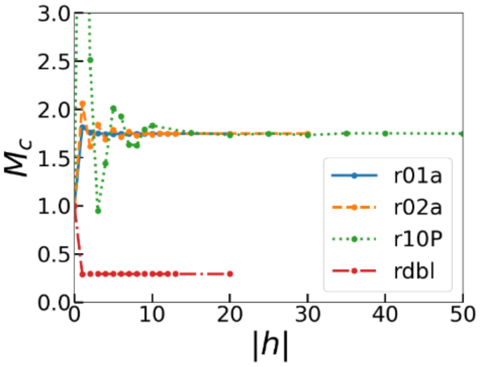

Figure 1. The $|\boldsymbol{h}|$ dependence of M$_c$(Madelung constant). (solid, blue r01a) $R = r_{FC}$; (dashed orange r02a) $R = r_{FC}/2$; (dotted green r10P) $R = r_{FC}/10$; (dash-dotted red rdbl) $R = 2r_{FC}$

We also find the linear relation between XPS binding energy and $1/r_{FC}$ of F. Kawamoto et al. measured inorganic fluorides and found the binding energies linearly depended on the $1/r_{FC}$.[8] This is due to the linear relation between the binding energy and the V_{int}(F), as shown in Figure 3. The V_{int}(F) is a potential created by the surrounding ions. The chemical shift of F$^-$ is determined by the Coulombic interaction, eV_{int}(F). The linear line in Figure 4 shows the relation of $\Delta E_B = e\,V_{int}$(F). The deviation from the linear line may be due to the polarization or charge transfer effects.

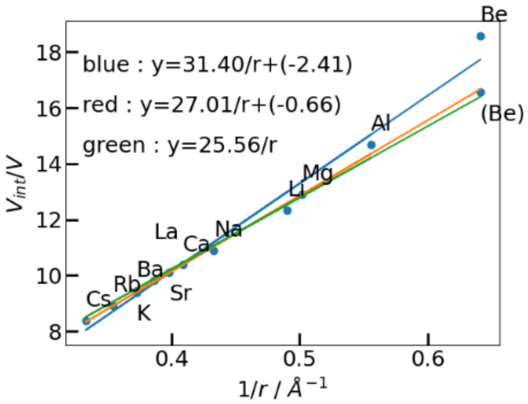

Figure 2 V$_{int}$ dependence on $1/r$. Blue, red, and green lines correspond to linear fit lines of all data and the data without BeF$_2$ data, a linear line fitted with intercept =0 V of the data without BeF$_2$ data.

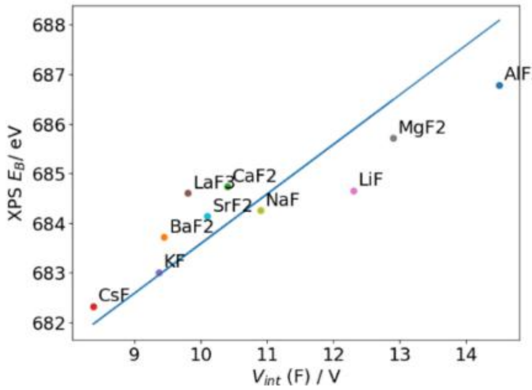

Figure 3 F 1s binding energy (eV) and V_{int}(F). Blue line is the $E_B = V_{int}$ (F) + (673.6 ± 1.8)

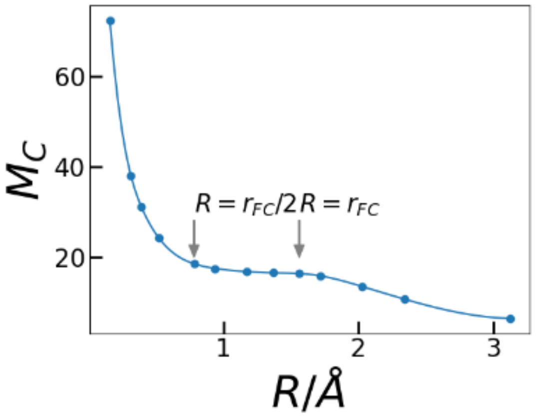

Figure 4 M_c dependence of BeF$_2$ on $1/r_{FC}$.

5. Conclusions

The chemical shift in binding energy of F1s is studied. It is related to the electrostatic potential at F position exerted by the surrounding ions, V_{int}(F) . $\Delta E_B = e\,V_{int}$(F) + (673.6 ± 1.8), where we find V_{int}(F) =

$\frac{M_{anion}e}{4\pi\epsilon_o r_{FC}}$ and $M_{anion} = 1.77$.

Associated Content

Supporting information is available free of charge at the J-Stage, Data https://jstagedata.jst.go.jp/.

Acknowledgements

The work is based on results obtained from a project, JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

[1] D. Shibata, Doctoral dissertation **2025**. *Ritsumeikan University.*
[2] K. Siegbahn, *ESCA Applied to Free Molecules*. Editor, North-Holland**,** Publishing Company, **1970**.
[3] Q. C. Johnson, D. H. Templeton, *J. Chem. Phys.* **1961**, *34*, 2004.
[4] W. L. Jolly, *The Principle of Inorganic Chemistry*. Editor, McGraw-Hill Book Company, **1976**.
[5] P. P. Ewald, *Annal. Phys,* **1921**, *369*, 253.
[6] R. M. Pratt, *J. Kejurut.* **2001**, *13*, 21.
[7] D. Argyriou, C. Howard, *Aust, J. Phys.***1992**, *45*, 239.
[8] Y. Kawamoto, K. Ogura, M. Shojiya, M. Takahashi, K. Kadono, *J,Fluorine Chem.* **1999**, *96*, 135.

Table 1 Summary of the samples with crystal structures, space group and bond distance. Vint is an electrostatic potential at F site.

Compound	Lattice structure	NC	Space Group	Bond distance /Å	V_{int}/V**	V_{int}(F)/V**	V_{int}(Ca)/V**	Madelung Const* (from reference [4])
LiF	NaCl	6	Fm-3m	2.04	-12.3	12.3	-12.3	1.747(1.747)
NaF	NaCl	6	Fm-3m	2.31	-10.9	10.9	-10.9	1.747(1.747)
KF	NaCl	6	Fm-3m	2.68	-9.37	9.37	-9.37	1.747(1.747)
RbF	NaCl	6	Fm-3m	2.83	-8.91	8.91	-8.91	1.747(1.747)
CsF	NaCl	6	Fm-3m	3.01	-8.38	8.38	-8.38	1.747(1.747)
BeF_2	Cubic	2	P1	1.56	-56.4 (-29.2)***	18.6 (16.6)***	-24,4 (-24.5)***	1.555 (1.478)***
MgF_2	Rutile	3	$P4_2$/mnm	1.99	-22.2	12.9	-22.2	1.593(1.6053)
CaF_2	CaF_2	4	Fm-3m	2.446	-19.3	10.4	-19.3	1.679(1.68)
SrF_2	CaF_2	4	Fm-3m	2.511	-18.8	10.1	-18.8	1.679(1.68)
BaF_2	CaF_2	4	Fm-3m	2.68	-17.6	9.45	-17.6	1.679(1.68)
LaF_3		2.34	P-3c1	2.47	-57.32	9.81	-27.1	1.55
AlF_3		2	R-3c	1.80	-32.9	14.5	-32.9	1.488

* Dependence of reduced Madelung Potential(M') is $U = -M'\frac{q_F q_{cation}(1+q_{cation})e^2}{2r_{FC}} = -M_c\frac{e^2}{r}$
** In order to adjust the unit to MKSA, the values are multiplied by 14.4(=$e/4\pi\epsilon_0$)
*** $R = r_{FC}$