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Expansion of the Madelung Parameters of Non-Cubic Structures as a Function of the Ratio of Two Lattice Parameters

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A new method is described to express the Madelung parameter of a structure with a non-cubic Bravais lattice as a function of a lattice parameter by means of a power series expansion. The method is derived for the case of a cubic lattice which is tetragonally distorted. The generalization to other crystal structures is shown. For illustration the method is applied to the rutile and cadmium iodide structures.

Introduction

In this paper a method is described to find an analytical expression of the Madelung parameters of non-cubic structures in terms of the ratio of two lattice parameters. Such an expression is useful, if the variation of the Madelung energy of a structure with two lattice parameters has to be considered as a function of one lattice parameter, while the other is kept constant. A problem of that kind arises, for instance, if the lattice energy has to be minimized with respect to one particular lattice parameter.

There is a further advantage of this method: once the expansion coefficients for a definite structure are computed, the Madelung constants of all compounds of this structure with the same parameter u but with different axial ratios may be evaluated simply by summing the series.

As an illustration, the Madelung parameters of the rutile and the cadmium iodide structures as a function of c/a have been calculated. The coefficients given in Table 2 can therefore be used to evaluate very quickly and conveniently the Madelung constants of all compounds with rutile or cadmium iodide structures as far as the parameters u agree with those assumed in this calculation (Table 1).

Method of calculation

The Madelung energy of an ionic crystal lattice can be written in the form

$$U_M=\frac{e_0^2N_A}{a}\frac{1}{2}\sum_i\sum_j z_iz_j\Psi(\mathbf{r}_i-\mathbf{r}_j)\,, \qquad (1)$$

where e_0 is the elementary charge, N_A is Avogadro's number, and z_i the valency of ion i at the position $\mathbf{r}_i$ of the unit cell. The sums over i and j extend over all ions of the basis.

$\Psi(\mathbf{r}_i-\mathbf{r}_j)$ are lattice sums which are defined by:

$$\Psi(\mathbf{r}_i-\mathbf{r}_j)=\sum_k\frac{1}{|\mathbf{R}_k-\mathbf{r}_i+\mathbf{r}_j|}\,. \qquad (2)$$

Summation is performed over all vectors $\mathbf{R}_k$ of the infinite real lattice.

For $\mathbf{r}_i=\mathbf{r}_j$ the self potential $\Psi(\mathbf{0})$ is obtained, where the term for $\mathbf{R}_k=\mathbf{0}$ is excluded from the summation:

$$\Psi(\mathbf{0})=\sum_{\substack{k\\ \mathbf{R}_k\neq\mathbf{0}}}\frac{1}{|\mathbf{R}_k|}\,. \qquad (3)$$

The Madelung parameter M_a, based on the lattice parameter a,

$$M_a=\frac{Ua}{z^2e_0^2N_A} \qquad (4)$$

can be written according to (1) in the form:

$$M_a=\frac{1}{2}\sum_i\sum_j\frac{z_iz_j}{z^2}\Psi(\mathbf{r}_i-\mathbf{r}_j)\,, \qquad (5)$$

where z is the smallest absolute value of the valencies z_i. It will be shown that in the case of a tetragonal distortion of a cubic lattice with fixed atomic positions the Madelung energy and the Madelung parameter can be expanded in a series of powers of the parameter

$$\alpha=1-\left(\frac{a}{c}\right)^2. \qquad (6)$$

The Madelung parameter M_a then takes the form:

$$M_a=\frac{a}{c}\sum_{m=0}^{\infty}\alpha^mM_a^{(m)}\,, \qquad (7)$$

where the coefficients $M_a^{(m)}$ are independent of the axial ratio a/c. The power series expansion (7) is convergent for $|\alpha|<1$, which is equivalent to $a/c<\sqrt{2}$.

However, this method is not only applicable if a tetragonal distortion of a cubic structure is considered, which is assumed here for convenience, but for all distortions where a lattice parameter is varied keeping the other lattice parameters and the atomic positions constant.

The lattice sums $\Psi(\mathbf{r})$ (2) have to be transformed into rapidly converging series. They can be written as a sum over the reciprocal lattice (Ewald, 1921):

$$\Psi(\mathbf{r}) = \frac{4\pi}{\Omega} \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} \, . \tag{8}$$

In this equation $\mathbf{q}_l$ may be written as:

$$\mathbf{q}_l = 2\pi(l_1\mathbf{b}_1 + l_2\mathbf{b}_2 + l_3\mathbf{b}_3) \, , \tag{9}$$

where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are the fundamental translations of the reciprocal lattice, and analogously:

$$\mathbf{r} = p_1\mathbf{a}_1 + p_2\mathbf{a}_2 + p_3\mathbf{a}_3 \, , \tag{10}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the fundamental translations of the real lattice. Ω is the volume of the (tetragonal) unit cell. The summation extends over all vectors of the (infinite) reciprocal lattice, where the term for $\mathbf{q}_l = \mathbf{0}$ has to be omitted.

If the tetragonal unit cell is considered to result from a distortion of a cubic cell with the same atomic positions and the same lattice parameter a, (8), with (6), can be expressed as:

$$\begin{aligned} \Psi(p_1,p_2,p_3) &= \frac{4\pi}{\Omega}\left(\frac{a}{c}\right) \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_{l1}^2 + q_{l2}^2 + (a^2/c^2)q_{l3}^2} \\ &= \frac{4\pi}{\Omega}\left(\frac{a}{c}\right) \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2[1-\alpha(q_{l3}^2/q_l^2)]} \, . \end{aligned} \tag{11}$$

In this equation Ω, $\mathbf{q}_l$, and $\mathbf{r}$ refer to the undistorted cubic structure.

The expression in (11) can be expanded in a series of powers of α:

$$\Psi(p_1,p_2,p_3) = \frac{4\pi}{\Omega}\left(\frac{a}{c}\right) \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} \sum_{m=0}^{\infty} \alpha^m (q_{l3}^2/q_l^2)^m \, . \tag{12}$$

If θ_l designates the angle between the vectors $\mathbf{q}_l$ and $\mathbf{q}_{l3}$ then q_{l3}^2/q_l^2 is given by:

$$(q_{l3}^2/q_l^2) = \cos^2 \theta_l \tag{13}$$

and (12) takes the form:

$$\begin{aligned} \Psi(p_1,p_2,p_3) &= \frac{4\pi}{\Omega}\left(\frac{a}{c}\right) \sum_{m=0}^{\infty} \alpha^m \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} \cos^{2m} \theta_l \\ &= \left(\frac{a}{c}\right) \sum_{m=0}^{\infty} \alpha^m \Psi^{(m)}(p_1,p_2,p_3) \, . \end{aligned} \tag{14}$$

This equation leads to an expression for the Madelung energy:

$$U_M = \frac{e_0 N_A}{c} \sum_{m=0}^{\infty} \alpha^m \tfrac{1}{2} \sum_i \sum_j z_i z_j \times \Psi^{(m)}(p_{1i}-p_{1j}, p_{2i}-p_{2j}, p_{3i}-p_{3j}) \, , \tag{15}$$

and for the Madelung constant:

$$\begin{aligned} M_a &= \frac{a}{c} \sum_{m=0}^{\infty} \alpha^m \tfrac{1}{2} \sum_i \sum_j \frac{z_i z_j}{z^2} \times \psi^{(m)}(p_{1i}-p_{1j}, p_{2i}-p_{2j}, p_{3i}-p_{3j}) \\ &= \frac{a}{c} \sum_{m=0}^{\infty} \alpha^m M_a^{(m)} \, , \end{aligned} \tag{16}$$

with the usual relation (4) between these two quantities.

To calculate the lattice sums (14), $\cos^{2m} \theta_l$ is expanded in Legendre polynomials (Sneddon, 1956):

$$\begin{aligned} \cos^{2m} \theta_l &= \sum_{n=0}^{m} a_{2n} P_{2n}(\cos \theta_l) \\ a_{2n} &= \frac{4n+1}{2} \int_{-1}^{1} x^m P_{2n}(x) \mathrm{d}x \\ &= (4n+1)2^{2n} \frac{(2m)!(m+n)!}{(m-n)!(2m+2n+1)!} \, , \end{aligned} \tag{17}$$

thus obtaining:

$$\begin{aligned} \Psi^{(m)}(p_1,p_2,p_3) &= \frac{4\pi}{\Omega} \sum_{n=0}^{m} (4n+1)2^{2n} \\ &\times \frac{(2m)!(m+n)!}{(m-n)!(2m+2n+1)!} \sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} P_{2n}(\cos \theta_l) \, . \end{aligned} \tag{18}$$

The lattice sums $\sum_l \exp(i\mathbf{q}_l \, . \, \mathbf{r}) P_{2n}(\cos \theta_l)/q_l^2$ have been formulated by Nijboer & De Wette (1957). They only exist for $\mathbf{r} \neq \mathbf{0}$:

$$\begin{aligned} &\sum_l{}' \frac{\exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} P_{2n}(\cos \theta_l) \\ &= \frac{1}{\Gamma(n+1)} \left[\sum_l{}' \frac{\Gamma(n+1, q_l^2/4\varepsilon^2) \exp(i\mathbf{q}_l \, . \, \mathbf{r})}{q_l^2} P_{2n}(\cos \theta_l) \right. \\ &\quad \left. + \frac{(-1)^n a^3}{4\pi^{3/2}} \sum_l \frac{\Gamma(n+\frac{1}{2}, \varepsilon^2 |\mathbf{r}_l - \mathbf{r}|^2)}{|\mathbf{r}_l - \mathbf{r}|} P_{2n}(\cos \Theta_l) - \frac{\delta_{n0}}{4\varepsilon^2} \right] , \end{aligned} \tag{19}$$

where $\mathbf{r}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$. $\Gamma(n,x)$ is the incomplete gamma function and Θ_l the angle between the vector $\mathbf{r}_l - \mathbf{r}$ and the z axis of the coordinate system. The numerical value of the lattice sum (19) does not depend on the parameter ε, which, however, has a relatively strong influence on the convergence of both series and which should be chosen dependent on the shape of the unit cell. For a cubic or nearly cubic cell a value of $\varepsilon \simeq \sqrt{\pi}$ should be appropriate.

The lattice sums $\Psi(\mathbf{0})$ (self potential) may be evaluated by means of Hund's (1935) identity:

$$\begin{aligned} &n\Psi(np_1, np_2, np_3) \\ &= \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} \sum_{k=0}^{n-1} \Psi\left(p_1 + \frac{i}{n}, p_2 + \frac{j}{n}, p_3 + \frac{k}{n}\right), \quad n > 0 \, . \end{aligned} \tag{20}$$

For $n=2$ and $\mathbf{r} = \mathbf{0}$ the self potential is obtained:

$$\begin{aligned} \Psi(0,0,0) &= \Psi(0,0,\tfrac{1}{2}) + \Psi(0,\tfrac{1}{2},0) + \Psi(\tfrac{1}{2},0,0) + \Psi(0,\tfrac{1}{2},\tfrac{1}{2}) \\ &+ \Psi(\tfrac{1}{2},0,\tfrac{1}{2}) + \Psi(\tfrac{1}{2},\tfrac{1}{2},0) + \Psi(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \, . \end{aligned} \tag{21}$$

In using this method to calculate the Madelung constants of a series of crystals of one type of structure which differ only in the ratios of two lattice parameters, one should take the mean value of the axial ratios of the substances investigated as origin of the expansion in order to obtain optimum convergence of the series (15) and (16).

This formalism can be applied to non-cubic structures if one proceeds as follows:

The components of the three fundamental translations of the structure under consideration are written as columns which are then combined to form the Bravais matrix A:

$$\mathsf{A}=\begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{pmatrix}. \qquad (22)$$

If the vectors $\mathbf{r}$ and $\mathbf{r}_l$ of the real lattice are considered as columns and the vectors $\mathbf{q}_l$ of the reciprocal lattice as rows, $\mathbf{r}$ has to be replaced by $\mathsf{A}\mathbf{r}$ ($\mathbf{r}_l$ by $\mathsf{A}\mathbf{r}_l$) and $\mathbf{q}_l$ by $\mathbf{q}_l\mathsf{A}^{-1}$ in the above mentioned equations to overcome the restriction to cubic Bravais lattices.

Applications and results

To demonstrate the capability of this method, the Madelung parameters (5) of the rutile and cadmium iodide structures have been calculated as a function of c/c_0. In case of the rutile structure and of the cadmium iodide structure, the axial ratio c/a of rutile and the axial ratio of a hypothetical compound with hexagonal close packing, respectively, were chosen as origin of the expansion in a series of powers of α with $\alpha=1-(c_0/c)^2$; c_0 is the length of the c axis in the above mentioned substances.

For any compound with rutile or cadmium iodide structure and with the parameter u, given in Table 1, the Madelung constant M_a may be calculated according to:

$$M_a=\frac{c_0}{c}\sum_{m=0}^{\infty}\alpha^m M_a^{(m)}, \qquad (23)$$

where $c_0=0{\cdot}64395\ a$ (rutile) or $c_0=1{\cdot}633\ a$ (cadmium iodide). The structural data on which the calculations are based are given in Table 1. The coefficients $M_a^{(m)}$ of the expansion up to $m=10$ are shown in Table 2.

Table 1. *Lattice parameters of rutile* (*Wyckoff*, 1965) *and of a hypothetical* CdI_2*-like structure with hexagonal close packing*

	Rutile	CdI_2-like
Symmetry	tetragonal $P4/mnm$	trigonal $P\bar{3}2/m1$
a (Å)	4·59373	
c (Å)	2·95812	
c_0/a	0·64395	1·633
u	0·3053	0·25
Z	2	1
Positions	Ti 2(a): $0, 0, 0$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ O 4(f): $u, u, 0$ $\bar{u}, \bar{u}, 0$ $u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}$ $\frac{1}{2}-u, u-\frac{1}{2}, -\frac{1}{2}$	Cd 1(a): $0, 0, 0$ I 2(d): $\frac{1}{3}, \frac{2}{3}, u$ $\frac{2}{3}, \frac{1}{3}, \bar{u}$

Table 2. *Coefficients* $M_a^{(m)}$ *for rutile and* CdI_2*-like structures*

m	Rutile	CdI_2-like
0	11·2635098	6·1731884
1	3·6798138	0·8523917
2	1·7790991	−0·9284454
3	1·5389700	−1·8819179
4	1·5996582	−2·4752279
5	1·6875960	−2·8653720
6	1·7406053	−3·1366386
7	1·7530071	−3·3363966
8	1·7333760	−3·4915026
9	1·6920092	−3·6174671
10	1·6375068	−3·7234901

For the rutile structure the Madelung constant can be reproduced by this expansion in the range of approximately $0{\cdot}57<c/a<0{\cdot}75$, corresponding to $|\alpha|=|1-(c_0/c)^2|<0{\cdot}27$, with a relative error of less than 10^{-7}. This range covers almost all known crystals with rutile structure. However, the parameter u is not strictly constant for all these substances, as is assumed here with $u=0{\cdot}3053$, but varies between approximately 0·300 and 0·307. For rutile itself the Madelung constant M_a is given by the constant term $M_a^{(0)}$ in the expansion (23) and has a value of 11·2635098.

For the cadmium iodide structure c/a can be varied between 1·45 and 1·9, corresponding to $|\alpha|<0{\cdot}27$, without resulting in a relative error greater than 10^{-7}. Therefore the Madelung constants of many crystals may be calculated by means of a single formula, assuming that the parameter u is 0·25. The Madelung constants given in Table 3 are evaluated with the coefficients of Table 2.

Table 3. *Madelung constants* M_a *for some crystals with cadmium iodide structure*

Lattice parameters according to Wyckoff (1965), $u=0{\cdot}25$ assumed for all substances.

	a	c	α	M_a
CaI_2	4·48 Å	6·96 Å	−0·1048668	6·3861126
$CoBr_2$	3·68	6·12	0·0358044	6·0903778
CoI_2	3·96	6·65	0·0543739	6·0450969
$FeBr_2$	3·74	6·17	0·0201824	6·1272148
FeI_2	4·04	6·75	0·0447269	6·0688278
GeI_2	4·13	6·79	0·0134186	6·1428210
$MgBr_2$	3·81	6·26	0·0121895	6·1456352
MgI_2	4·14	6·88	0·0344024	6·0937297
$MnBr_2$	3·82	6·19	−0·0155886	6·2075068
MnI_2	4·16	6·82	0·0078204	6·1555850

However, the expansion for the Madelung constant obtained by the method presented here can be used in a wider range, if only fair precision is required. To obtain Figs. 1 and 2, which show the Madelung constants M_a, based on the lattice parameter a, and M_{r_0}, based on the shortest cation–anion distance r_0, of the rutile and cadmium iodide structures as functions of c/a, only a few expansions were necessary to cover the whole range.

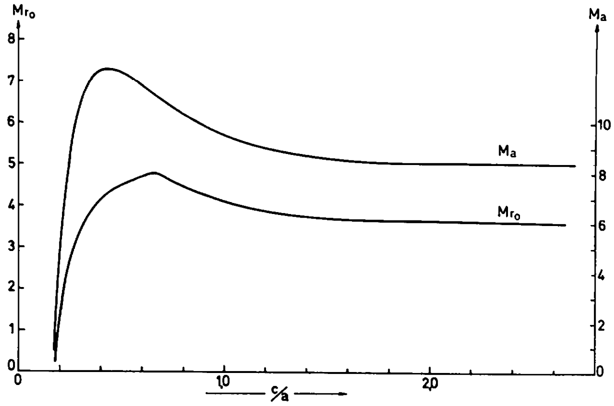

Fig. 1. Madelung constants M_a and M_{r_0} for the rutile structure as functions of c/a.

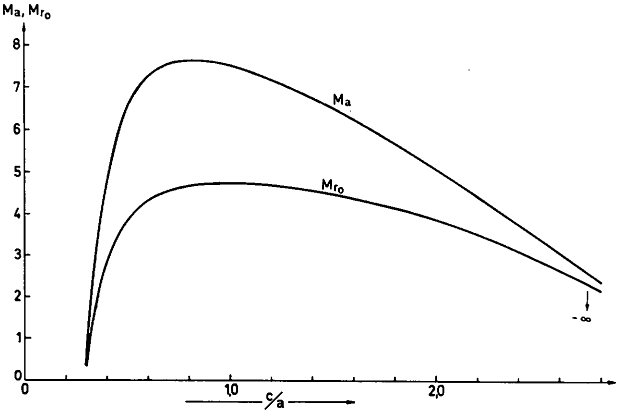

Fig. 2. Madelung constants M_a and M_{r_0} for the cadmium iodide structure as functions of c/a.

In case of the rutile structure, the vectorial interatomic distance which represents the smallest cation–anion distance, changes at $c/a=(8u-2)^{1/2}$ and is given by:

$$r_0=\begin{cases}[2(0\cdot5-u)^2+0\cdot25(c/a)^2]^{1/2} & \text{for } c/a\leq(8u-2)^{1/2}\\ u\sqrt{2} & \text{for } c/a\geq(8u-2)^{1/2}\,.\end{cases}$$

M_{r_0} has a maximum for an axial ratio where both distances are equal, which means that each metal atom is equidistantly surrounded by six O atoms (Hoppe, 1966):

$$(c/a)_{M_{r_0}=\max}=(8u-2)^{1/2}\quad u>0\cdot2793\,.$$

For $0\cdot25<u<0\cdot2793$, however, the maximum of M_{r_0} is not connected with the condition of six equal metal–oxygen distances, but coincides with the maximum of M_a. The maximum of M_a for the rutile structure with $u=0\cdot3053$ is at $(c/a)_{M_a=\max}=0\cdot43797$.

The maxima of M_a and M_{r_0} for the cadmium iodide structure are at $(c/a)_{M_a=\max}=0\cdot8170$ and $(c/a)_{M_{r_0}=\max}=0\cdot9822$, respectively.

The calculations have been carried out at the Computer Center of the Technical University of Vienna.

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