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# On the electrostatics of cubic crystals

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**Abstract.** The electrostatic potential in an ionic crystal is presented in terms of the zeroth-order MacDonal function by means of decomposition of the crystal lattice into sets of parallel lines with the periodic charge distribution with zero net charge within a period. The method is applied to the calculation of the Madelung constants of a series of standard cubic lattices, doped fullerenes and idealized Y–Ba–Cu–O crystals.

## 1. Introduction

The discovery of the high-temperature superconductivity of copper oxide ceramics has revived interest in the ionic crystal theory (see, e.g., [1, 2]). A new boom has arisen in connection with the recent synthesis of carbon clusters  $C_{60}$  of icosahedral symmetry. These clusters also form ionic crystals if doped with alkali metals. This type of compound—fullerenes—also manifests high-temperature superconductivity [3]. Superconducting systems such as  $K_3^+C_{60}^{3-}$  possess various body- or face-centred crystalline phases, and this has focused attention on the calculation of the electrostatic energy of different fullerite crystalline modifications [4].

The main problems of the calculation of the Madelung constants were solved many years ago as a result of the methods of Madelung [5], Epstein [6], Ewald [7] and others [8–11] and summarized in the comprehensive review by Tosi [12]. However, in reality, computer programs are still used [2, 4] but not explicit analytical expressions which allow one to observe the details of the potential formation.

Here our purpose is to present simple analytical formulae for the Madelung constants, vacancy potentials and electrostatic contributions to the crystal surface energy. The method used is similar to the Evjen [8] technique; however, the domain considered, the straight line with the total zero charge, is infinite. As a result of application of the Hund [13] lattice superposition principle the Madelung constants have a simple analytical form in terms of the zeroth-order MacDonal function. For the latter, simple interpolation formulae exist which ensure six-decimal accuracy (equation (9.86) of [14]).

## 2. Equations for the geometric factors of the potential

Let us calculate the potential of a set of charges  $\pm q$  situated on a straight line with a distance  $d$  between them. In the cylindrical coordinates  $\rho, z$  in units of  $d$  with the origin at  $+q$  which can always be chosen so that at  $-1 < z < 1$  the potential

$$V(\rho, z) = \frac{q\varphi(\rho, z)}{d} = q \sum_{k=-\infty}^{\infty} \frac{(-1)^k [\rho^2 + (k+z)^2]^{-1/2}}{d} \quad (1)$$

is an even periodic function. The period is equal to 2:

$$\varphi(\rho, z + 2) = \varphi(\rho, z) = \varphi(\rho, -z). \tag{2}$$

A substitution of  $k$  by  $k - 1$  leads to

$$\varphi(\rho, z + 1) = -\varphi(\rho, z) \tag{3}$$

from which it follows that

$$\varphi(\rho, \frac{1}{2}) = -\varphi(\rho, -\frac{1}{2}) = -\varphi(\rho, \frac{1}{2}) = 0. \tag{4}$$

Therefore the Fourier series for  $\varphi(\rho, z)$  is

$$\varphi(\rho, z) = \sum_{n=1}^{\infty} a_n(\rho) \cos(\pi n z) \tag{5}$$

where

$$a_n(\rho) = 2 \sum_{k=-\infty}^{\infty} \int_0^1 dz \frac{(-1)^k \cos(\pi n z)}{\sqrt{\rho^2 + (k + z)^2}} \tag{6}$$

vanish for  $n$  even and reduce to

$$a_{2l-1}(\rho) = 4 \int_0^{\infty} du \frac{\cos[\pi(2l-1)u]}{\sqrt{\rho^2 + u^2}} = 4K_0(\pi(2l-1)\rho) \tag{7}$$

for  $n$  odd according to equation (3.771.2) of [15], where  $K_0$  is the zeroth-order MacDonalld function. As a result the main electrostatic sum is

$$\varphi(\rho, z) = 4 \sum_{l=1}^{\infty} K_0(\pi(2l-1)\rho) \cos[(2l-1)\pi z] \tag{8}$$

(compare with equation (B18) of [12]). In fact, only a few terms remain in equation (8) as a consequence of the more than exponential decrease in the MacDonalld function, e.g.  $K_0(5\pi)$  is already less than  $5 \times 10^{-8}$ .

It is worthwhile to mention that for  $\rho = 0$  the left-hand side of equation (8) is reduced to

$$\varphi(0, z) = \beta(z) + \beta(-z) + 1/z \tag{9}$$

in spite of the fact that  $K_0(0)$  is infinite where according to [15]

$$\beta(z) = \sum_{k=1}^{\infty} (-1)^k (k + z)^{-1} = \frac{1}{2} \ln \left( \frac{\Gamma(\frac{1}{2}(z + 1))}{\Gamma(\frac{1}{2}z)} \right) \tag{10}$$

and  $\Gamma$  is the Euler gamma function. In order to find the potential in the lattice node it is necessary to subtract the self-interaction term  $1/z$ . Then

$$\left( \varphi(0, z) - \frac{1}{z} \right)_{z=0} = 2 \sum_{k=1}^{\infty} \frac{(-1)^k}{k} = -2 \ln 2. \tag{11}$$

With the condition that  $\varphi(0, 0)$  describes the node potential we shall define

$$\varphi(0, 0) = -2 \ln 2. \tag{12}$$

The generalization of equation (7) (see equation (3.771) of [15])

$$\int_0^\infty du \frac{\cos(au)}{\sqrt{(b^2 + u^2)^{2n+1}}} = \frac{a^n}{(2n - 1)!! b^n} K_n(ab) \tag{13}$$

allows us to consider in a similar way the potential of the multipole chain, etc. It should be mentioned that numerical values of  $K_0(x)$  are given by the six-order polynomial over  $2/x$  multiplied by  $\exp(-x)$  with an accuracy of  $10^{-7}$  [14] while

$$\beta\left(\frac{1}{2}\right) = \pi/2 \quad \beta\left(\frac{1}{3}\right) = \ln 4 + \pi/\sqrt{3} \quad \beta\left(\frac{2}{3}\right) = \pi/\sqrt{3} - \ln 4 \tag{14}$$

$\beta\left(\frac{1}{4}\right)$ ,  $\beta\left(-\frac{1}{4}\right)$ , etc, are known 'exactly' [15].

Similarly to equation (2) the potential of a set of identical parallel lines is also a periodic function of  $z$  with the same period 2. Three sets denoted by  $L^\pm(d, r/d)$  and  $M(d, r/d)$  will be used below. Here  $r$  is a period AD of the square network in the perpendicular plane ABCD which the parallel lines mentioned (AA', BB', ...) intersect at the vertices of the network. In the first case ( $L^+$ ) the charges at the vertices A, B, C and D are identical; in the second ( $L^-$ ) they differ in the neighbouring vertices as well as in the third case ( $M$ ). However, in the latter case the charges are identical along each 'vertical' line (figure 1). For  $L^+(d, r/d)$  it is sufficient to find the potential at the points of the prism AEFNLM. The potential vanishes on its upper face, changing from the maximal values on the base mainly according to the cosine law (equation (8)) with the addition of an increasing number of higher harmonics when approaching the vertex A. We shall be interested in the potential values mainly at the node A, at the edge middle E and at the face centre F and more rarely at the points P, Q and R (figure 1). If the potential is presented in the form

$$V = g(u)q/d \quad u = r/d \tag{15}$$

the geometrical factors will be

$$g_A(u) = \sum_{s,t=-\infty}^\infty \mathcal{R}\left(u\sqrt{s^2 + t^2}\right) \tag{16}$$

$$g_E(u) = \sum_{s,t=-\infty}^\infty \mathcal{R}\left(u\sqrt{\left(s - \frac{1}{2}\right)^2 + t^2}\right) \tag{17}$$

$$g_F(u) = \sum_{s,t=-\infty}^\infty \mathcal{R}\left(u\sqrt{\left(s - \frac{1}{2}\right)^2 + \left(t - \frac{1}{2}\right)^2}\right) \tag{18}$$

and for the arbitrary point  $(x, y)$  on the base

$$g_{x,y}(u) = \sum_{s,t=-\infty}^\infty \mathcal{R}\left(u\sqrt{(s-x)^2 + (t-y)^2}\right) \tag{19}$$

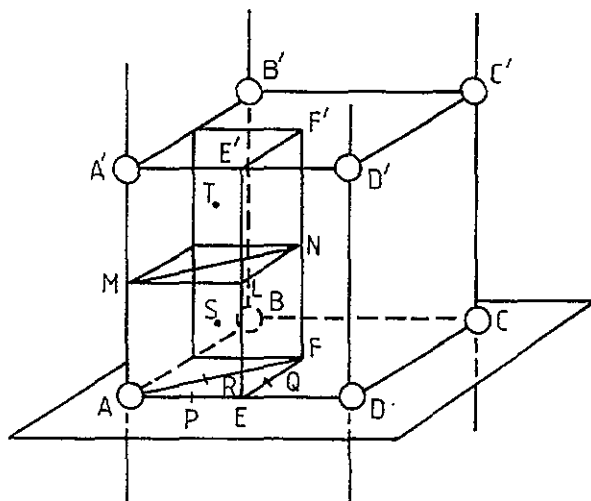


Figure 1. The main points of the cubic cell.

where  $x$  and  $y$  are measured in units of  $r$  and the notation

$$\mathcal{R}(\rho) = \varphi(\rho, 0) = 4 \sum_{l=1}^{\infty} K_0(\pi(2l-1)\rho) \quad (20)$$

has been used.

It is interesting that, in  $L^-(d, u)$ , new quantities in the geometrical factors  $h(u)$  do not appear:

$$h_A(u) = \sum_{s,t=-\infty}^{\infty} (-1)^{s+t} \mathcal{R}\left(u\sqrt{s^2+t^2}\right) = g_A(2u) + g_F(2u) - 2g_E(2u) \quad (21)$$

$$h_E(u) = h_F(u) = h_Q(u) = 0. \quad (22)$$

To consider the system  $M(d, u)$  we first calculate the potential from a horizontal plane situated at the distance  $td$  from A at this point. Since the horizontal lines of alternating charges intersect the vertical plane at the points  $(s, t/u)$ ,

$$V_A(t) = \frac{q}{du} \sum_{s=-\infty}^{\infty} (-1)^s \mathcal{R}\left(\sqrt{s^2 + \frac{t^2}{u^2}}\right). \quad (23)$$

Therefore the geometrical factors  $m(u)$  will be

$$m_A(u) = \frac{d}{q} \sum_{t=-\infty}^{\infty} V(t) = \frac{1}{u} \sum_{s,t=-\infty}^{\infty} (-1)^s \mathcal{R}\left(\sqrt{s^2 + \frac{t^2}{u^2}}\right) \quad (24)$$

$$m_M(u) = \frac{1}{u} \sum_{s,t=-\infty}^{\infty} (-1)^s \mathcal{R}\left(\sqrt{s^2 + \frac{(t - \frac{1}{2})^2}{u^2}}\right). \quad (25)$$

In the same manner we obtain a new expression for  $h_A(u)$  which is convenient for small  $r$  and large  $d$  in contrast with equation (21) which is applicable in the opposite case:

$$h_A(u) = \frac{d}{q} \sum_{t=-\infty}^{\infty} (-1)^t V(t) = \frac{1}{u} \sum_{s,t=-\infty}^{\infty} (-1)^{s+t} \mathcal{R} \left( \sqrt{s^2 + \frac{t^2}{u^2}} \right). \quad (26)$$

There are many other useful identities between the introduced quantities. If we add to the set  $L^+(d, u)$  its copy  $L_F^+(d, u)$  with the origin at F or subtract it, a similar set  $L^\pm(d, u/\sqrt{2})$  rotated by  $45^\circ$  results:

$$L^+(d, u) \pm L_F^+(d, u) = L^\pm(d, u/\sqrt{2}). \quad (27)$$

Simultaneously points F, E, R, P and Q turn into B, F, E, R and '-R' in the new set. Equating suitable geometrical factors we have

$$g_A(u) + g_F(u) = g_A(u/\sqrt{2}) \quad 2g_E(u) = g_F(u/\sqrt{2}) \quad (28)$$

and

$$2g_R(u) = g_E(u/\sqrt{2}) = \frac{1}{2}g_F(\frac{1}{2}u) \quad g_P(u) + g_Q(u) = g_R(u/\sqrt{2}) = \frac{1}{2}g_E(\frac{1}{2}u). \quad (29)$$

Similarly to equation (21),

$$g_A(u) = g_A(2u) + g_F(2u) + 2g_E(2u) \quad g_A(u) - g_F(u) = h_A(u/\sqrt{2}). \quad (30)$$

In particular cases from equations (21) and (28),

$$h_A(\sqrt{2}) = g_A(2) - g_F(2) \quad (31)$$

and from definitions (23), (24) and (16)–(18) the equalities

$$m_A(\frac{1}{2}) = 2g_A(2) - 2g_E(2) \quad m_M(\frac{1}{2}) = 2g_E(2) - 2g_F(2) \quad (32)$$

result while equation (26) gives

$$\begin{aligned} 2h_A(\sqrt{2}) &= \sqrt{2} \sum_{s,t=-\infty}^{\infty} (-1)^s \left[ \mathcal{R} \left( \sqrt{s^2 + 2t^2} \right) - \mathcal{R} \left( \sqrt{s^2 + \frac{1}{2}(2t-1)^2} \right) \right] \\ &= m_A(1/\sqrt{2}) - m_M(1/\sqrt{2}). \end{aligned} \quad (33)$$

Another type of identity follows if we note that the vertical plane in set  $L^+(d, 1)$  is formed by  $45^\circ$ -rotated lines of alternating charges and only every second line gives a non-zero potential on the line AD. Since the distance between these lines is  $\sqrt{2}$ , it is clear that we deal with the set  $M(d, \sqrt{2})$  rotated around the horizontal axis by  $45^\circ$ . Therefore

$$g_A(1) = m_A(\sqrt{2}) \quad g_E(1) = m_M(\sqrt{2}) \quad (34)$$

and from the definitions (24) and (25) it follows that

$$g_A(1) = \frac{1}{2}[m_A(1/\sqrt{2}) + m_M(1/\sqrt{2})]. \quad (35)$$

Solving equations (35) and (33) for  $m_A(1/\sqrt{2})$  and  $m_M(1/\sqrt{2})$  and taking into account equations (30) and (31) we have

$$m_A(1/\sqrt{2}) = 2[g_A(2) + g_E(2)] \quad m_M(1/\sqrt{2}) = 2[g_E(2) + g_F(2)]. \quad (36)$$

Thus it is evident from equations (30)–(32) and (36) that the key quantities are  $g_A(2)$ ,  $g_E(2)$  and  $g_F(2)$  for which special notation will be used:

$$a = g_A(2) = -2 \ln 2 + 16[K(4) + K(8) + K(16) + 2K(20)] = -1.370683$$

$$b = g_F(2) = 16[K(2) + 2K(10) + 2K(18)] = 0.109706 \quad (37)$$

$$c = g_E(2) = 8\{K(1) + 2[K(5) + K(9) + K(13) + K(17)]\} = 0.243293$$

where for brevity it was denoted

$$K_0(\pi\sqrt{x}) = K(x). \quad (38)$$

Sometimes we shall also need

$$g_P(2) = 4\{K(\frac{1}{4}) + 2[K(\frac{9}{4}) + K(\frac{49}{4}) + K(\frac{17}{4}) + K(\frac{41}{4}) + K(\frac{73}{4})]$$

$$+ 4[K(\frac{25}{4}) + K(\frac{65}{4})]\} = 0.829914 \quad (39)$$

$$g_Q(2) = 8\{K(\frac{5}{4}) + K(\frac{13}{4}) + K(\frac{29}{4}) + K(\frac{37}{4}) + K(\frac{53}{4}) + K(\frac{61}{4}) + 2K(\frac{45}{4})\}$$

$$= 0.170079.$$

It is worthwhile to mention the relation  $g_P(2) + g_Q(2) = 0.99999$ .

### 3. Madelung constants for standard cubic lattices

Now we can turn to the calculation of the Madelung constants of real lattices.

#### 3.1. NaCl type

It is evident that this lattice with Na atoms situated at points A (figure 1) and Cl at points B, A', D, etc, is simply the set  $L^-(\frac{1}{2}R, 1)$  where  $R$  is the lattice constant. Therefore the Madelung constant according to equations (21) and (37) is

$$\alpha(\text{NaCl}) = -2h_A(1) = 4c - 2a - 2b = 3.495126 \quad (40)$$

in accordance with [12]. The corresponding constant for a single NaCl layer results from potential (23)  $V(O)$ :

$$\alpha(\text{NaCl, layer}) = f = 2\{2 \ln 2 + 8[K(1) + 2K(9) - K(4) - K(16)]\} = 3.231084. \quad (41)$$

As a result the surface (100) Madelung constant is

$$\alpha(\text{NaCl, surface}) = \frac{1}{2}[f + \alpha(\text{NaCl})] = 3.363105 \quad (42)$$

which corresponds to the results in [16].

The plane layer  $\text{CuO}_2$  in Ba-La-Cu-O ceramics may be considered as a set of +4 charges formed by all atoms situated above and under Cu in a cell and of -2 charges of O. Thus +2q must be placed at A (figure 1), -q at B and D while C remains empty. This means that the layer considered is a superposition of the NaCl layer and its 45°-rotated copy with the lattice constant  $d\sqrt{2}$ . Then

$$f(\text{Cu}) = -(\frac{1}{2} + \sqrt{2}/4)f = -2.757903 \quad f(O) = f$$

$$f(\text{vac}) = -(\frac{1}{2} - \sqrt{2}/4)f = -0.473181. \quad (43)$$

3.2. Perovskite ( $BaBiO_3$ ) type

Here the doubled (Bi) positive charges are at A, B, C and D, a single (Ba) charge at N, and negative (O) charges at the edge middles E, M, E', etc (figures 1 and 2). Therefore subtracting from this lattice the set  $L^-(\frac{1}{2}R, \sqrt{2})$  we reduce the charges at A, A', etc, twice, annihilate the charges at the vertical edge middles and bring the positive charges from the cell centre N to the face centre F, i.e. transform the lattice into the set  $M(R, \frac{1}{2})$ . Symbolically

$$L(BaBiO_3) = L^-(\frac{1}{2}R, \sqrt{2}) + M(R, \frac{1}{2}). \tag{44}$$

Equating the geometrical factors according to equation (44), we have

$$\begin{aligned} g(\text{Bi}) &= 2h_A(\sqrt{2}) + m_A(\frac{1}{2}) = 4a - 2b - 2c = -6.188\,730 \\ g(\text{Ba}) &= 2h_A(2) + m_M(\frac{1}{2}) = 2a + 2c - 4b = -2.693\,604 \\ g(\text{O}) &= 2h_F(\sqrt{2}) - m_A(\frac{1}{2}) = 2c - 2a = 3.227\,952 \\ g(\text{O}') &= -2h_A(\sqrt{2}) + m_M(\frac{1}{2}) = g(\text{O}) \\ g(\text{vac, F}) &= -2h_A(\sqrt{2}) + m_A(\frac{1}{2}) = 2b - 2c = -0.267\,174 \\ g(\text{vac, P}) &= -g(\text{vac, Q}) = 2h_R(\sqrt{2}) + m_P(\frac{1}{2}) = 2[g_P(2) - g_Q(2)] = 1.319\,670 \end{aligned} \tag{45}$$

where equations (22), (30)–(32) and (39) and  $m_P(\frac{1}{2}) = 0$  have been taken into account. The Madelung constant for the perovskite lattice is

$$\alpha(BaBiO_3) = \frac{1}{2}[3g(\text{O}) - g(\text{Ba}) - 2g(\text{Bi})] = -2g(\text{Bi}) = 12.377\,460 \tag{46}$$

since according to equation (45) the identity

$$3g(\text{O}) + 2g(\text{Bi}) - g(\text{Ba}) = 0 \tag{47}$$

holds.

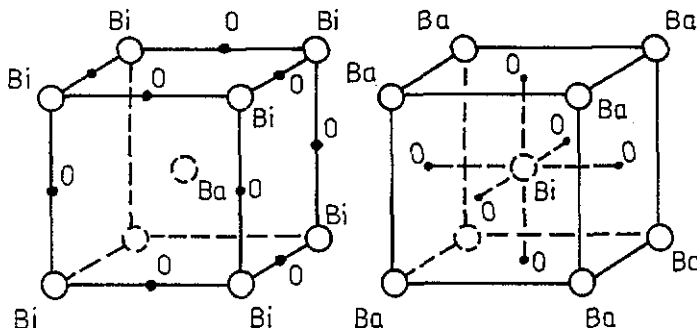


Figure 2.  $BaBiO_3$  cell with origins at Bi and Ba.



### 3.3. CsCl type

In this lattice, Cs atoms are at A, B, C and D and Cl at N (figure 1). If we subtract the set  $L^+(\frac{1}{2}R, 2)$  with the origin at F, chlorine atoms move into the face centres and the set  $M(R, 1/\sqrt{2})$  appears. Thus

$$L(\text{CsCl}) = L^+(\frac{1}{2}R, 2) + M(R, 1/\sqrt{2}). \quad (48)$$

In the same manner as before,

$$g(\text{Cs}) = 2g_F(2) + m_A(1/\sqrt{2}) \quad g(\text{Cl}) = -2g_A(2) - m_M(1/\sqrt{2}). \quad (49)$$

Naturally from equations (36) and (37) it follows that

$$g(\text{Cl}) = -g(\text{Cs}) = -2(a + b + c) = 2.035\,368 \quad (50)$$

in complete agreement with [12]. Similarly we have

$$\begin{aligned} g(\text{vac, E}) &= 2g_E(2) + m_F(1/\sqrt{2}) = 2c = 0.486\,586 \\ g(\text{vac, F}) &= 2g_A(2) - m_A(1/\sqrt{2}) = -2c = -g(\text{vac, E}). \end{aligned} \quad (51)$$

Considering the superposition  $L(\text{BaBiO}_3) + kL(\text{CsCl})$  we deal with a perovskite crystal in which the relative charges of the Bi and Ba sites are  $2 - \frac{1}{2}k$  and  $1 + \frac{1}{2}k$ , i.e.  $k$  electrons are transferred from Ba to Bi. The new geometrical factors will be  $g(\text{Bi}) = -6.188\,130 + 2.035\,368k/2$ ,  $g(\text{Ba}) = -2.693\,604 - 2.035\,368k/2$ ,  $g(\text{O}) = 3.227\,952 - 0.486\,586k/2$ . Therefore the electrostatic energy of the elementary cell

$$-\frac{1}{2}[(2 - \frac{1}{2}k)g(\text{Bi}) + (1 + \frac{1}{2}k)g(\text{Ba}) - 3g(\text{O})]$$

is maximal for  $k = 1.7172$  when the charges on Bi and Ba are 2.2828 and 3.7172 but not equal as they would be for two isolated charges with a fixed sum. The real structure of  $\text{BaBiO}_3$  corresponds to the maximal deviation from such an unstable charge distribution. For both trivalent cations this structure becomes less stable. For instance, in  $\text{LaCuO}_3$  the oxygen atoms move towards the Cu site and the lattice transforms into the  $R\bar{3}c$  symmetry type. Nevertheless the potentials  $V(\text{O}) = 21.89$  and  $V(\text{Cu}) = -38.48$  calculated for  $k = 1$  with the lattice constants of  $\text{LaCuO}_3$  do not deviate essentially from their values in the real crystal: 22.32 and  $-38.21$  [1]. A similar picture is observed for  $\text{La}_2\text{CuO}_4$  where the corresponding values are 22.21 and  $-28.0$  while in [1] they are 21.65 and  $-27.57$ .

### 3.4. $\text{CaF}_2$ , $\text{Cu}_2\text{O}$ and zincblende types

The application of the Hund lattice superposition principle enables us to calculate directly the geometric factors for the lattices mentioned from those already obtained. It is clear that the addition of the NaCl lattice with the origin at S (figure 1) and with the same minimal charge to the ZnS lattice transforms the latter into its copy with empty and full small cubes interchanged. As a result, S 'shifts' to the point T. Therefore

$$g(\text{T}) + g(\text{Cl}) = g(\text{S}). \quad (52)$$

A similar result is achieved if we subtract  $L(\text{CsCl})$  with the halved lattice constant from  $L(\text{ZnS})$ . However, in this case the transformed lattice is shifted by  $R\sqrt{3}/4$  along the main cube diagonal, and the positive charge appears at T:

$$g(\text{T}) + 2g(\text{Cs}) = g(\text{Zn}). \quad (53)$$

Simultaneously the centre of the small cube edge P transforms into a point equivalent to the face centre of this cube:

$$g(\text{P}) - 2g(\text{vac, E}) = g(\text{R}). \quad (54)$$

Naturally  $g(\text{S}) = -g(\text{Zn})$  as well as  $g(\text{R}) = -g(\text{P})$  since P and R take similar positions relatively to S and Zn. Now we can solve equations (52)–(54) and obtain, taking into account equations (40), (50) and (51),

$$g(\text{S}) = -g(\text{Zn}) = \frac{1}{2}g(\text{Cl}) - g(\text{Cs}) = -3(a + b) = 3.782\,931$$

$$g(\text{vac, T}) = -g(\text{vac, oct}) = -g(\text{Cs}) - \frac{1}{2}g(\text{Cl}) = -a - b - 4c = 0.287\,805 \quad (55)$$

$$g(\text{P}) = -g(\text{R}) = g(\text{vac, E}) = 2c = 0.486\,586.$$

Since the  $\text{CaF}_2$  lattice is a superposition of  $L(\text{ZnS})$  with its copy we immediately have

$$g(\text{Ca}) = -2g(\text{S}) = 6(a + b) = -7.565\,862$$

$$g(\text{F}) = g(\text{S}) + g(\text{T}) = -2g(\text{Cs}) = -4(a + b + c) = 4.070\,736 \quad (56)$$

$$g(\text{oct, vac}) = 2g(\text{vac, oct, ZnS}) = 2(a + b + 4c) = -0.575\,61.$$

The Madelung constant for this crystal is

$$\alpha(\text{CaF}_2) = g(\text{F}) - g(\text{Ca}) = 11.636\,598. \quad (57)$$

It is not difficult to note that, in contrast with ZnS, in  $\text{Cu}_2\text{O}$  the anions form a body-centred and not a face-centred lattice. From figure 2 it is clear that adding to  $\frac{1}{2}L(\text{ZnS})$  the perovskite lattice with the same minimal charge and Ba coincident with Zn transforms the ZnS lattice into the body-centred lattice with the doubled cation charge:

$$\frac{1}{2}L(\text{ZnS}) + \frac{1}{2}L(\text{BaBiO}_3) = -L(\text{Cu}_2\text{O}) \quad (58)$$

where the coefficients are attributed to the minimal charges in the corresponding lattices. As before, from equation (58) it follows that

$$g(\text{O}) = -g(\text{Zn}) - g(\text{Ba}) = -5a + b - 2c = 6.476\,535$$

$$g(\text{Cu}) = -g(\text{S}) = 3(a + b) = -3.782\,931$$

$$g(\text{E, vac, Cu}_2\text{O}) = -g(\text{vac, oct}) - g(\text{vac, E}) = -a + b - 6c = 0.020\,631$$

and

$$\alpha(\text{Cu}_2\text{O}) = g(\text{O}) - g(\text{Cu}) = 10.259\,466. \quad (59)$$

Thus we have demonstrated in detail how the technique proposed works in the case of traditional cubic lattices and gives for the Madelung constants the same results as have been tabulated in [12]. Now we shall consider some more actual examples.

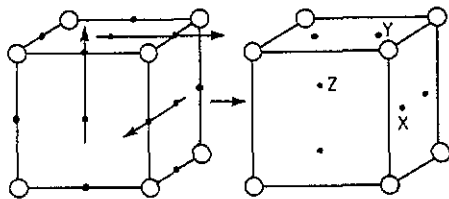


Figure 3. Transformation of the bcc type into the A15 type.

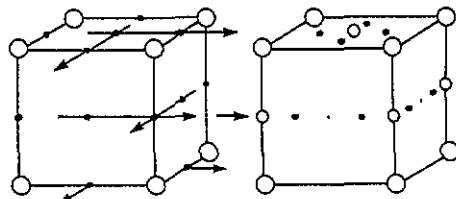


Figure 4. The first step of transformation of  $A_3^+ C_{60}^{3-}$  into  $A_4^+ C_{60}^{4-}$ .

#### 4. Potential geometrical factors in some fullerides and other crystals

The various crystalline modifications of fullerides  $A_3^+ C_{60}^{3-}$  are interesting examples to demonstrate the above technique. In the first case,  $C_{60}$  cages form a face-centred lattice (AA'LD) with the cations in the tetrahedral (S and T) and octahedral (E, E' and M) positions (figure 1). It is clear that this lattice is simply a superposition of  $L(\text{CaF}_2)$  and  $L(\text{NaCl})$  with the opposite signs. Then

$$\begin{aligned} g(C_{60}) &= -g(\text{Ca}) - g(\text{Na}) = -4(2a + 2b - c) = 11.060\,988 \\ g(A, \text{ tetr}) &= -g(\text{F}) = 4(a + b + c) = -4.070\,736 \\ g(A, \text{ oct}) &= -g(\text{oct, CaF}_2) + g(\text{Na}) = -12c = -2.919\,516. \end{aligned} \quad (60)$$

The next phase is a body-centred lattice of  $C_{60}$  while cations occupy the centres of the edges and of faces. From figure 2 we see that here  $L(A_3^+ C_{60}^{3-}) = \frac{1}{2}[L(\text{BaBiO}_3) + L'(\text{BaBiO}_3)]$ . Therefore,

$$\begin{aligned} g(C_{60}) &= -g(\text{Ba}) - g(\text{Bi}) = -6a + 6b = 8.882\,334 \\ g(A) &= -g(\text{O}) - g(\text{vac, F}) = 2a - 2b = -2.960\,778 \end{aligned} \quad (61)$$

and both positions of cations are equivalent here.

A more complicated situation arises in a  $Pm\bar{3}n$  lattice which is obtained from the preceding lattice by moving cations by  $R/4$  from the edge middles and from the face centres in the three mutually perpendicular directions shown by arrows in figure 3. One such motion is achieved by the subtraction of a properly oriented set  $L^+(\frac{1}{4}R, 4)$  with the origin at the edge middle. As a consequence of the presence of the large coefficient  $u = 4$  in equations (16)–(19), suitable sums can, in fact, be made to reduce to a single term. The initial geometrical factors for anion and for cation were  $-6a + 6b$  and  $-2g(\text{vac, Q}) = 2.639\,34$  according to equation (45). The displacement in the  $z$  direction adds to these the term  $4g_A(4) = 4[-2 \ln 2 + 16K(16)] = -5.5451$  for a cation at point Z, the term  $-4g_Q(4) = -32[K(5) + K(13)] = -0.013\,38$  for cations at points X and Y and the term  $-4g_E(4) = -32K(4) = -0.029\,332$  for the anion as follows from a comparison of figure 1 with figure 3. The coefficient 4 appears since the geometrical factors are attributed to  $R$  rather than to  $d$ . All three displacements in common contribute  $-12g_E(4)$  to the anion and  $4[g_A(4) - 2g_Q(4)]$  to each cation. Finally

$$g(C_{60}) = 8.794\,338 \quad g(A) = -2.932\,52. \quad (62)$$

The final example, the BCC lattice  $A_4^+C_{60}^{4-}$ , is obtained from the BCC lattice  $A_3^+C_{60}^{3-}$  by means of a two-stage shift. In the first stage, four shifts of the type already considered and indicated by arrows in figure 4 should be superposed. The appropriate contributions to the potentials are easily calculated as before in terms of the constants  $g_i(4)$ . The resulting lattice of the first stage is shown in figure 4. It remains only to move up by  $\frac{1}{2}R$  the unit negative charges from the middles of the horizontal faces and of the vertical edges, and this can be achieved by adding the lattice from figure 5 which is simply the set  $L^-(\frac{1}{2}R, \sqrt{2})$ . As a result the geometrical factors are

$$g(C_{60}) = 8(b - a - 2g_E(4)) = 11.725784 \quad (63)$$

$$g(A) = -3g(\text{vac}, Q) + 4[g_A(4) - g_P(4) - g_Q(4) + g_F(4)] = -2.068458$$

where

$$g_P(4) = 4[K(1) + K(9)] = 0.118167 \quad g_F(4) = 16K(8) = 0.000918. \quad (64)$$

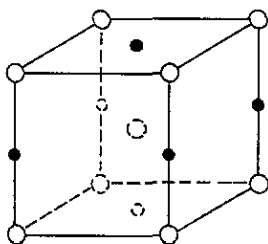


Figure 5. The point-charge distribution in an auxiliary cell.

From the factors given, it is not difficult to find the Madelung constants per cation which coincide with the results of the computer calculation [4] and, taking into account the internal anion energy [17], give the relative stabilities of the three phases considered in accordance with experiment [4].

#### 4.1. Idealized Y-Ba-Cu-O type

'Idealized' means that all atoms are situated at the lattice nodes and symmetry points, trivalent Cu at the edge cell planes and divalent Cu in the middle planes, and also that  $c = 3R$  and  $a = b = R$  (figure 6). A simple preliminary generalization of the basic equation (8) is necessary here. If within a period  $d$  there is an arbitrary distribution of  $p$  charges  $q_1, q_2, \dots, q_p$  placed at distances  $0 < a_1 < a_2 < \dots < a_p < 1$  (in units of  $d$ ) from the period origin, then by means of the same technique as before we obtain

$$V(\rho, z) = \sum_{k=-\infty}^{\infty} \sum_{s=1}^p \frac{q_s}{d\sqrt{\rho^2 + (z - k - a_s)^2}} = 2 \sum_{n=-\infty}^{\infty} Q_n K_0(2\pi n\rho) \exp(2\pi inz)/d \quad (65)$$

where

$$Q_n = \sum_{s=1}^p q_s \exp(-2\pi ina_s). \quad (66)$$

The infinite term  $K_0(0)$  is absent in equation (65) because the net cell charge  $Q_0 = \sum_{s=1}^p q_s$  vanishes, and we can rewrite  $V(\rho, z)$  in the real form

$$V(\rho, z) = 4 \sum_{n=1}^{\infty} K_0(2\pi n\rho) \sum_{s=1}^p \frac{q_s \cos[2\pi n(z - a_s)]}{d}. \quad (67)$$

For  $p = 2$ ,  $q_1 = q$ ,  $q_2 = -q$ ,  $a_1 = 0$ ,  $a_2 = \frac{1}{2}$  the coefficient  $Q_n = q[1 - (-1)^n]$  returns us to equation (8) written in terms of the doubled unit length. If the distances between charges are equal, i.e.  $a_s = (s - 1)/p$ ,  $Q_n$  is a periodic function of  $n$ :  $Q_{n+p} = Q_n$ .

A set of parallel lines of the above type with the smallest mutual distances  $ud$  will be denoted by  $L^{(p)}(d, u)$  with the following correspondence to the former notation:  $L^{(2)}(2d, \frac{1}{2}u) = L^+(d, u)$  where  $p$  in fact denotes the whole set of charges  $q_1, q_2, \dots, q_p$  and their positions. For the Y-Ba-Cu-O lattice the set  $L^{(6)}(3R, \frac{1}{3})$  with the following six charges will be necessary:  $q_1 = 1, a_1 = 0$ ;  $q_2 = 0, a_2 = \frac{1}{6}$ ;  $q_3 = -2, a_3 = \frac{1}{3}$ ;  $q_4 = 3, a_4 = \frac{1}{2}$ ;  $q_5 = -2, a_5 = \frac{2}{3}$ ;  $q_6 = 0, a_6 = \frac{5}{6}$ . Then  $Q_n = 1 + 3(-1)^n - 4 \cos(\frac{2}{3}\pi n)$ , and equation (65) reduces to

$$\begin{aligned} V(\rho, z) = & 8(K_0(4\pi/3\rho) \cos(4\pi/3z) - K_0(2\pi\rho) \cos(2\pi z) + K_0(8\pi/3\rho) \cos(8\pi/3z) \\ & + K_0(16\pi/3\rho) \cos(16\pi/3z) - K_0(6\pi\rho) \cos(6\pi z) \\ & + K(20\pi/3\rho) \cos(20\pi/3z))/R \end{aligned} \quad (68)$$

where  $\rho$  and  $z$  are measured in units of  $R$ , and the argument  $28\pi/3$  of the first omitted term exceeds  $4\pi$  for the smallest required distances  $\rho = \frac{1}{2}$ . As a result the expressions for the geometrical factors (16)–(19) continue to be valid for the set  $L^{(6)}$  if the function  $\mathcal{R}(\rho)$  from equation (20) is substituted by  $2\lambda(\rho) - \mu(\rho)$  for the points in the bottom plane in figure 6 and by  $-\lambda(\rho) + \mu(\rho)$ ,  $-\lambda(\rho) - \mu(\rho)$ ,  $2\lambda(\rho) + \mu(\rho)$  for the next three atomic planes, respectively, where

$$\begin{aligned} \lambda(\rho) &= 4[K_0(4\pi/3\rho) + K_0(8\pi/3\rho) + K_0(16\pi/3\rho) + K_0(20\pi/3\rho)] \\ \mu(\rho) &= 8K_0(2\pi\rho) + 8K_0(6\pi\rho). \end{aligned} \quad (69)$$

Now we turn to the lattice potentials. Since the number of important points is rather large, we outline briefly only the general decomposition of the lattice without explicit calculation of the geometrical factors for all non-equivalent atomic sites. The latter is already a simpler problem. Naturally the decomposition procedure is ambiguous; only the condition  $Q_0 = \sum_{s=1}^p q_s = 0$  is guaranteed at each step.

If we introduce at the set symbols  $L$ ,  $M$ , etc, also the notation of the origin position (rotation of the plane axes by  $45^\circ$  is recognized because of the presence of  $\sqrt{2}$  in the arguments), figure 7 becomes self-explanatory. In the final step, besides  $L^{(6)}(3R, \frac{1}{3})$  (shown explicitly), three plane sets  $P$  of parallel lines describing displacements of the indicated charges to the central axis have appeared. The volume sets here are unnecessary since the distance between similar planes is six times the displacement length, and the planes do not interact. Thus the identity

$$\begin{aligned} L(\text{YBa}_2\text{Cu}_3\text{O}_7) = & 2M_A(R, \frac{1}{2}) - 2M_M(R, 1/\sqrt{2}) + 2P_E(\frac{1}{2}R, 2) + 2P_A(R/\sqrt{2}, 2) \\ & + 2P_G(R/\sqrt{2}, 2) + L_F^{(6)}(3R, \frac{1}{3}) \end{aligned} \quad (70)$$

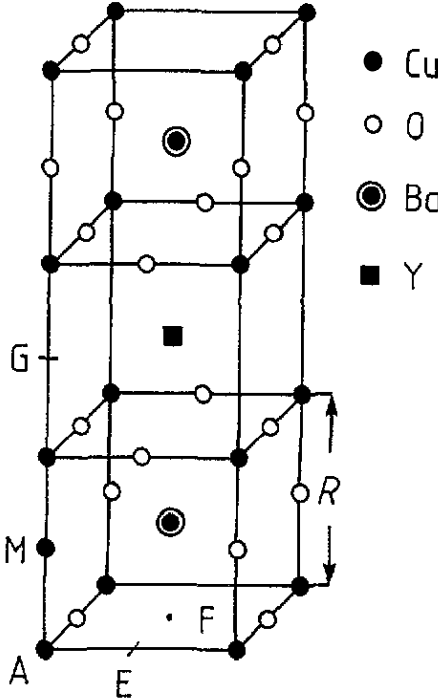


Figure 6. The unit cell of the idealized Y-Ba-Cu-O lattice.

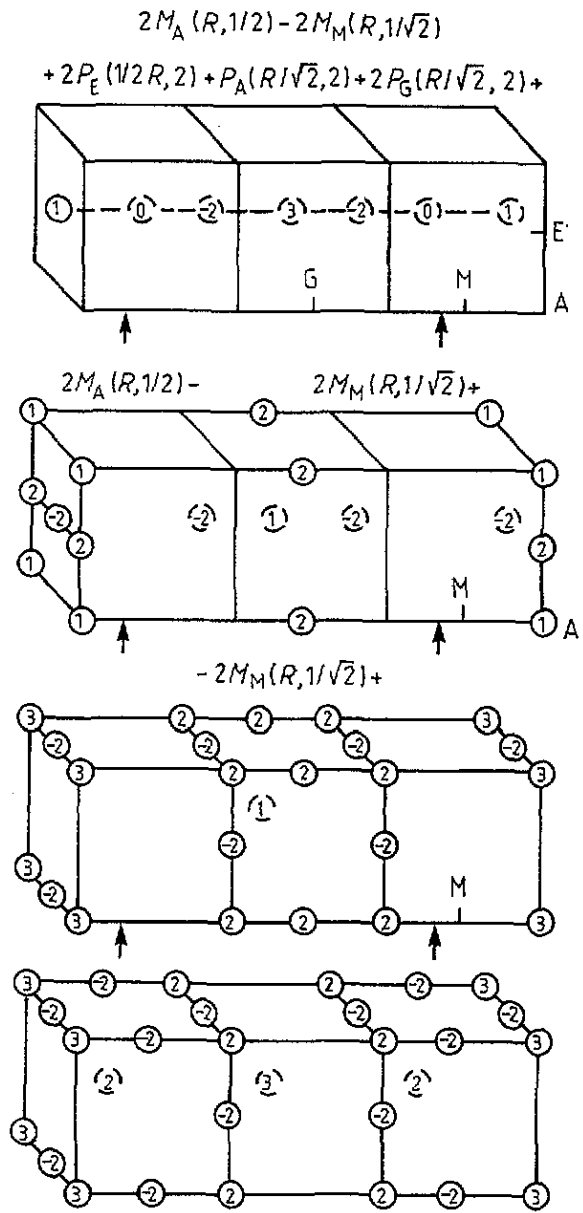


Figure 7. The decomposition procedure for Y-Ba-Cu-O.

allows one to calculate geometrical factors for each atom by means of equations (16)–(19) and (69).

In a similar way we can optimize the valences of Cu atoms in non-equivalent positions when their charges may be assumed to be  $3 - q$  and  $2 + \frac{1}{2}q$ . This requires us only to add to equation (70) the set  $L_A^{(3)}(3R, \frac{1}{3})$  with the corresponding potential

$$8 \sum_{n=1}^{\infty} \frac{K_0((2\pi/3)n\rho) \cos((2\pi/3)nz) \sin^2((\pi/3)n)}{3R} \quad (71)$$

and to determine  $q$  from the minimum-energy condition. However, for the latter only the electrostatic argument is insufficient.

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