CALCULATION OF STABILITY RANGES OF CHARGED ALKALI HALIDE CLUSTERS

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE
STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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Listen to the glad shouts of victory
in the tents of God's people:
"The LORD'S mighty power has done it"
ps 118:15

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Tesfaye Demissie

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ABSTRACT

The critical Coulomb explosion number, i.e., the lower bounds of particle size required to stabilize a multiply charged alkali halide cluster against Coulomb explosion were calculated using a simple Coulomb potential. The magnitude of the charge ranges from 2 to 10. The influence of sign and position of the charges were assessed. The critical Coulomb explosion number increases with increasing number of charges on the clusters. The critical coulomb explosion number and the charge of the clusters are linearly related with a good correlation.

The binding energies of the most tightly bound neutral isomers of $(NaCl)_n$, n=2-12, were calculated using a simple Coulomb potential. The stability order of the various isomers of a given cluster size is predicted using binding energy as a criteria. These results are compared with other works which employ refined but computationally expensive potential models. The agreement is good.

1. INTRODUCTION

Clusters are sub-microscopically small atomic aggregates with physical properties so unlike other forms of matter[1] that they have been called "the fifth state of matter"[2]. A variety of clusters have been studied: heterogeneous clusters(alkali halides[3], rare gases doped with large organic molecules[4], and rare gases doped with alkali halides[5]), alkali[6] and transition metals[7-10] and non-metal clusters[11].

Clusters of atoms or ions are of special interest in material science because materials composed of these so called "nanocrystals" have unusual properties[1]. Clusters are intermediates in the transition between gaseous and condensed phases which make them an interesting subject of experimental and theoretical investigations.

Sattler et al[12] have observed that doubly ionized atom clusters appear in time of flight mass spectra only if the clusters contain more than a critical number of atoms. This number was reported as 30 for Pb_n, 20 for $(NaI)_n$ and 52 for Xe_n. In these clusters, the two positive charges generated by electron bombardment are likely to move to opposite sides of the cluster which then explodes into singly charged fragments as long as the Coulomb repulsion energy is greater than the binding energy.

The stability of a charged alkali halide cluster comes to an end at a lower limit of size when the Coulomb repulsion energy exceeds the binding energy of the cluster. Theoretical computation of the binding energy of such clusters, therefore, enables one to estimate the critical number of atoms which should be present for the charged cluster to be stable. The main aim of this work is to predict these lower limits of size for multiply charged alkali halide clusters.

2. THEORETICAL BACKGROUND

The recent interest in small particles of alkali halides can be attributed in part to

(1) the simple ionic binding character of alkali halide solids,

(2) the relative ease with which molecular scale particles or clusters of these materials can be formed and studied, and

(3) to the availability of straightforward but accurate model potential for calculating the energetic interaction within the clusters. The following discussion concerns itself with some aspects of alkali halide clusters.

2.1 Structure

Atom clusters are too small to be observed even with an electron microscope. For a knowledge of their structure one must rely on total energy calculations. For covalent and metallic clusters it is simply not possible to define a two-body interaction potential which is independent of cluster size and shape. Such a potential does exist, however, for interactions between rare gas atoms. The extremely localized nature of the closed shell rare gas wavefunctions is responsible for this great simplification. Alkali halide clusters also have closed shell electronic configurations and should, therefore, be suitable candidates for structural studies.

Because the binding energy in alkali halides is almost purely ionic, an alkali halide cluster is best viewed as being composed of ions held together by Coulomb forces. The mechanism of binding are thus independent of the overall charge on the cluster. While the ions in alkali halide clusters can be arranged in many metastable configurations there will always be one lowest energy or ground state configuration. Finding the ground state configuration for an alkali halide cluster is the same as finding the minimum of its potential energy function.

Let r_i be the position of the i^{th} ion in the cluster, $V_{ij}(r_i, r_j)$ the potential energy between the ions i and j and E_i^s the self energy of the ion i measured relative to the self energy of the isolated ion. Then the total potential energy of a cluster of n ions, as a function of position, is

$$V(r_1, ..., r_n) = 1/2 \, \Sigma_{i=j, j=1, i\neq j}^{n} V_{ij} + \Sigma_{j=1}^{n} E_i^s \text{..........(1}$$

For alkali halides, there are two important models for the ion-ion potentials: the rigid core model and the shell model.

2.1.1 The rigid core model

For the rigid core model[5],

$$V_{ij}^{rigid} = q_i q_j / r_{ij} + A_{ij} e^{-r_{ij}/\rho} \text{..........(2}$$

$$E_i^{s,rigid} = 0$$

where r_{ij} is the distance separating the point charges q_i and q_j. The first term is the Coulomb interaction between ions and the second term, the Born-Meyer potential, reflects the mutual repulsion due to the overlap of the ions' wavefunctions. The constants A_{ij} and ρ are determined empirically based on properties of the bulk solid. The parameter ρ is related, not surprisingly, to the compressibility of the particular compound under investigation. It is a measure of the "firmness" of the ions, and can be deduced from data on crystal compressibilities. The other empirical factor A_{ij} can be eliminated by requiring the first derivative of the lattice energy of the bulk crystal to be zero at the equilibrium interionic spacing.

2.1.2 The shell model

The shell model[13-15], due to Rittner[13], introduces a polarizability αi for each ion. This gives rise to an electric dipole moment μi at each ion. With this addition to the rigid core model, the potential energy terms are of the form:

$$V_{ij}^{shell} = q_i q_j / r_{ij} + A_{ij} e^{-r_{ij}^{eff}/\rho} - q_i(\mu_j . r_{ij})/r_{ij}^3 - q_j(\mu_i . r_{ij})/r_{ij}^3 - 3(\mu_i . r_{ij})(\mu_j . r_{ij})/r_{ij}^5 + (\mu_i . \mu_j)/$$

$$+\mu_i^2/2\alpha_i^2 + \mu_j^2/2\alpha_j^2 \text{..........(3)}$$

$$E_{ij}^{s.shell} = \mu_i/2\alpha_i^2 + \mu_j/2\alpha_j^2 \text{..........(4)}$$

$$r_{ij}^{eff} = r_{ij} - \mu_i/Q_i + \mu_j/Q_j \text{..........(5}$$

The first term in equation (3) represents the Coulomb interaction between the point charges q_i and q_j separated by a distance r_{ij}. The second term is short range Born-Meyer repulsive interaction. The third and fourth terms give the interaction between point charges q_i and the dipole moment μ_j of atom j. The next two terms represent the dipole-dipole interaction and the last two terms the self energy of the dipoles. The total energy of the clusters is found by summing over i and j and counting interaction pairs only once.

When calculating the Born-Meyer potential, r_{ij} is replaced with r_{ij}^{eff} since the polarization of each ion induces a shift of the centre of charge with respect to the nucleus of the ion so that the effective distance for the Born-Meyer potential is different from that of the electrostatic interactions. Q_i can be thought of as a shell charge.

While using both models, the total energy must be minimized to find the stable configurations. The calculational procedure is as follows. First, One has to decide how many ions are to be contained in a cluster. These ions are placed anywhere in space. Then, they are allowed to move, in the calculation, under the constraint that for each movement the total energy must be lowered, until it is not possible to move any ion in any direction without increasing the total energy. Then a stable or at least metastable configuration has been found.

2.1.3 Neutral Clusters

The stable configurations of $(MX)_n$ clusters (n=2-16) calculated using the rigid core model[3] is shown in figure 1. The parameters used in the calculation are appropriate for NaCl.

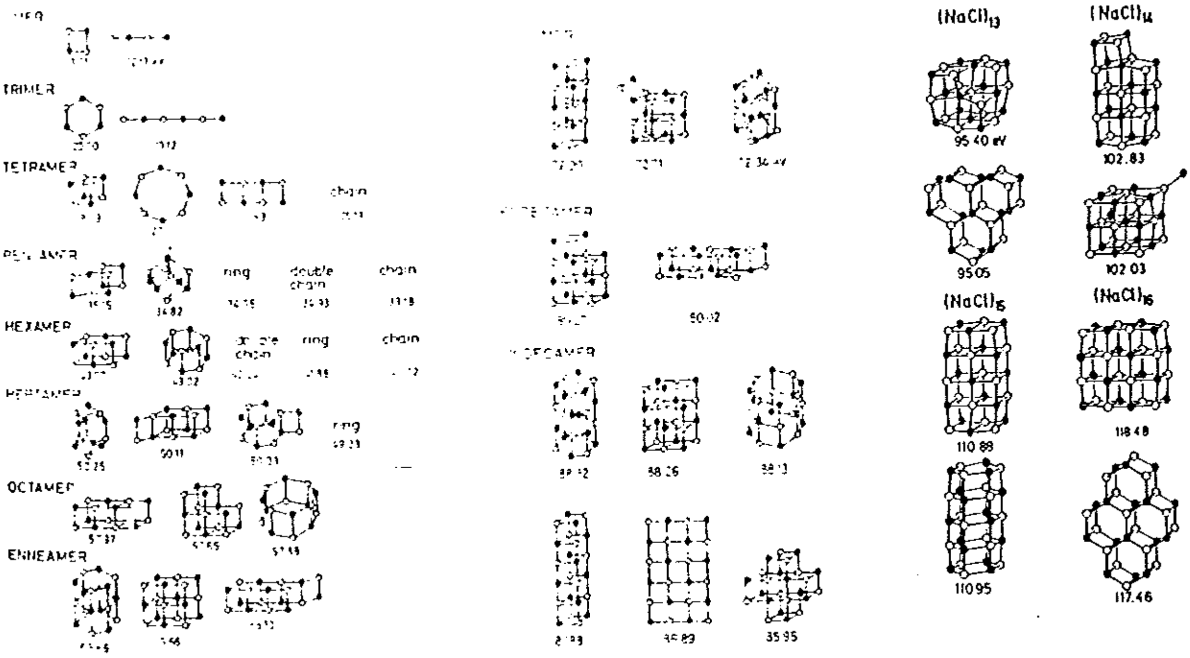


Fig. 1. The equilibrium configuration and corresponding binding energies of NaCl clusters predicted using the rigid core model.

Because of the long range forces between ions, close packed structures are not necessarily the most favourable as they are for the rare gas clusters. For example, a linear chain of rare gas atoms is not stable since there is no force preventing the end atom from rolling around its neighbour until it makes contact with a second nearest neighbour. Such motion is prevented in ionic clusters by repulsion of the second nearest neighbour which has the same charge. Similarly, the compact rectangular planar trimer is unstable even though positive ions make contact only with negative ions. The repulsion between the second nearest neighbours causes the rectangular trimer to open up forming a ring of six atoms with alternating charge. This six ring proves to be one of the most stable sub-units or building blocks of ionic clusters. For example, a stack of six ring units such as is possible for the 12, 18, and 24 atom clusters, often proves to be the most stable isomer of a given size.

Clearly for smaller clusters, structures resembling a portion of an NaCl crystal lattice are not always energetically favoured. However as the number of molecules in the cluster increases, the face centred cubic structure becomes more and more prevalent.

Phillips and co-workers[16], have calculated the lowest energy configuration of neutral $(NaCl)_n$ clusters n ranging from 2 to 5 using the shell model. Their results are shown in figure 2.

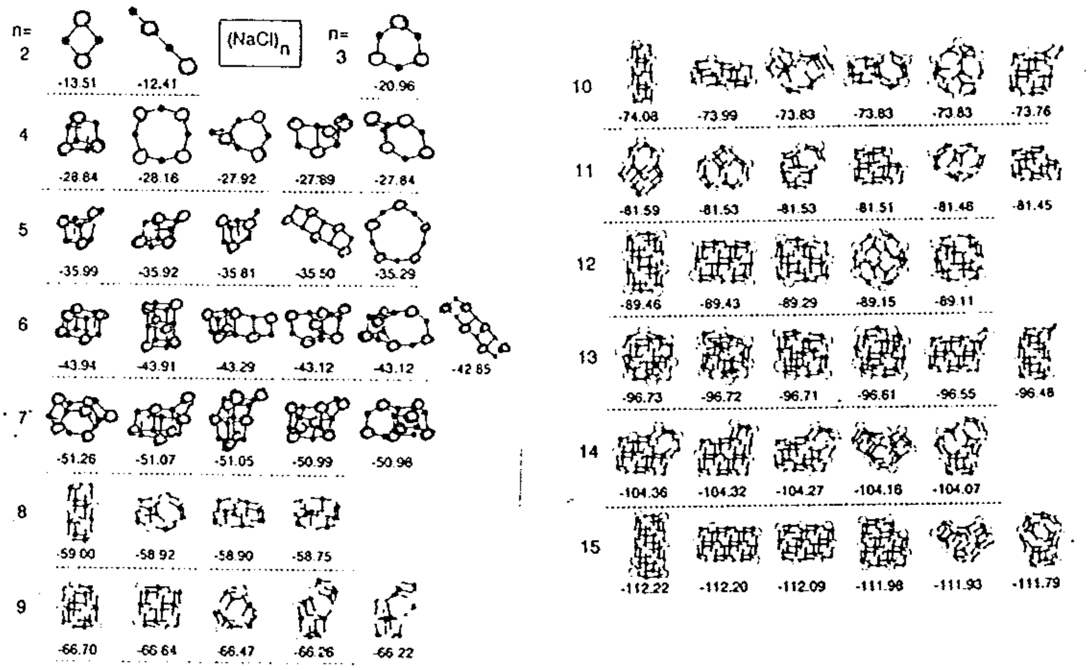


Fig. 2. The equilibrium configuration and corresponding binding energies of NaCl clusters predicted using the shell model.

Recently sodium chloride clusters, $(NaCl)_n$ (n=1-6, 8, 9, 12, 15, 18, and 32) were systematically investigated using ab initio methods[17]. Energetically stable geometries are shown in figure 3.

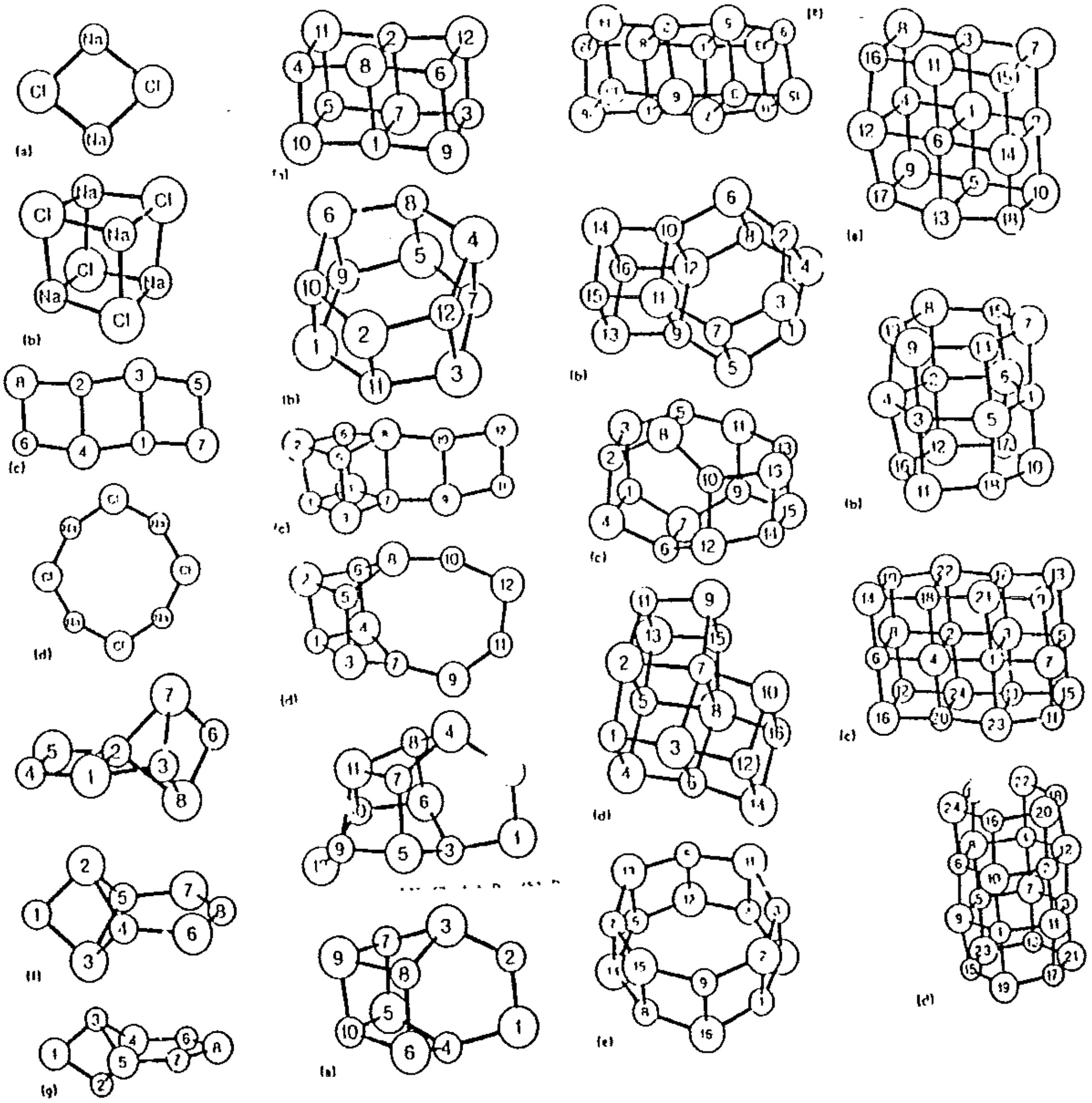


Fig. 3. Stable configurations of NaCl clusters predicted by ab initio calculations.

These results reveal that the energetically most stable isomers of even the smaller clusters show a marked preference for geometries which are fragments of the solid state lattice.

2.1.4 Mass Spectra

Mass spectroscopy experiments have shown that large clusters do exist in appreciable concentrations under non-equilibrium conditions[12, 18-23]. The intensity of a given line in a mass spectrum is influenced by many factors; the stability of the neutral clusters entering the ionization chamber, the cross section of the ionization, the probability of fragmentation and finally the stability of the ionized products.

2.1.5 Singly Charged Clusters

Clusters of alkali halides observed in the mass spectrometers usually do not contain equal number of alkali and halide atoms. This fact merely reflects the high degree of ionicity in these materials and can be explained as follows. If all the electrons in the cluster are localized, the electrons most easily removed can be thought of as belonging to the halide ions. After ionization the neutral halide atom interacts with the remaining ions in the cluster through a relatively weak monopole-induced dipole term. This interaction is insufficient to compete with the large amount of energy converted to vibrational motion during the ionization process. The neutral halide atom is lost resulting in a cluster with composition $M_nX_{n-1}^+$.

Stable configurations of clusters having compositions $M_nX_{n-1}^+$ have been calculated using the rigid core model[3]. The parameters used in equation 2 have been fitted to the crystalline NaCl lattice constant and compressibility(fig.4).

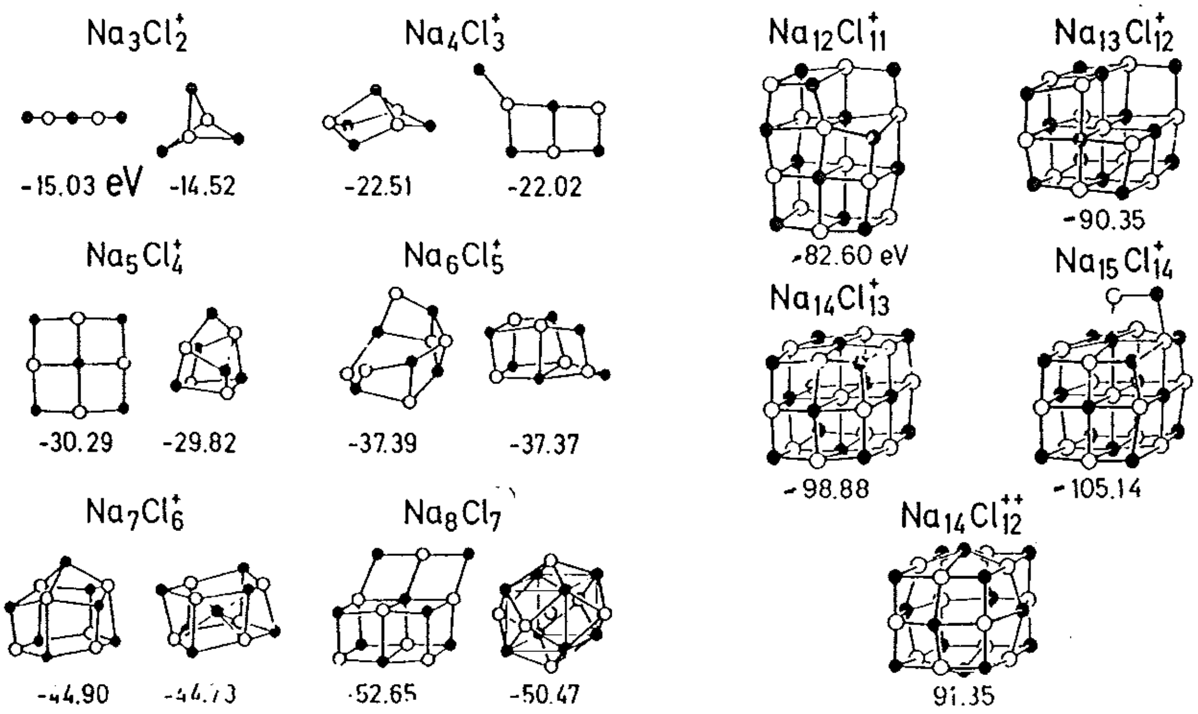


Fig. 4. Stable configurations of $NaCl_{n-1}^+$ clusters based on the rigid core model.

The negative of the calculated total energy per molecule for the most stable form of clusters ranging in size from 6 to 32 atoms is shown in figure 5. For such small clusters there is a general increase in binding energy per molecule with increasing cluster size simply because of increase in average co-ordination number. The curve for charged clusters

Table 1. Number of molecules in clusters with high stability.

structure	$(NaCl)_n$	$Na_nCl_{n-1}^+$	structure	$(NaCl)_n$	$Na_nCl_{n-1}^+$
3x3x1		5	4x4x2	16	
3x3x2	9		4x4x3	24	
3x3x3		14	4x4x4	32	
3x3x4	18		4x4x5	40	
3x3x5		23			
3x3x6	27				

The geometries and binding energies of singly charged NaCl clusters of the form $Na(NaCl)_n^+$ and $(NaCl)_nCl^-$, n=2 to 14 were calculated by Phillips and coworkers[16] using the shell model(fig.6).

Fig. 6. Configurations and binding energies of Na(NaCl)$_n^+$ and (NaCl)$_n$Cl$^-$ clusters based on the shell model.

The positive and negative cluster ions, $Na(NaCl)_n^+$ and $(NaCl)_nCl^-$ do not always share the same lowest energy configurations so that interchanging Na+ and Cl^- ions in one ground state configuration does not necessarily produce the ground state of the oppositively charged cluster ion. For n=5, 6, 7, 9, 10, 11, and 12 the ground state configurations are different. These configurational differences and the small increased binding energy of the negatively charged cluster ions are due to differences in the sizes and polarizabilities of the small Na^+ and large Cl^- ions.

Mass spectroscopic experiments with Cs halides reveal that a highly stable cluster must contain only paired electrons[11]. It has been shown that if only one chlorine atom is built into the cluster, mass peaks corresponding to $(Cs_2Cl)^+$, $(Cs_4Cl)^-$, $(Cs_6Cl)^-$ etc., are particularly strong. However, if two chlorine atoms are built into the cluster, an odd number of Cs atoms are preferred, i.e, the peaks due to $(Cs_3Cl_2)^+$, $(Cs_5Cl_2)^-$ etc., are strong. Therefore if the number of Cs plus the number of Cl atoms is odd, the peak in the mass spectrum is strong.

This can be understood if all electrons are required to occur in pairs. Each Cs and Cl atom has one unpaired electron. Therefore, the total numbers of atoms must be odd, since one electron has been removed from each of these positively charged clusters.

2.1.6 Doubly Charged Clusters

Most doubly ionized covalent molecules are not stable because the Coulomb repulsion energy between the two positive holes exceed the molecular binding energy. Only a few highly bound covalent molecules have been found, for example $(HCl)^{2+}$, $(HI)^{2+}$, $(N_2)^{2+}$, $(O_2)^{2+}$, $(NO)^{2+}$, $(CO)^{2+}$, $(CO_2)^{2+}$, and $(NH_3)^{2+}$[24]. Few cases of alkali halides have been reported.

Sattler el al[12] have observed that doubly ionized atom clusters appear in time-of-flight mass spectra only if the clusters contain more than a critical number of atoms. In the mass spectrum of doubly charged sodium chloride clusters, $(NaI)_n^{++}$ are expected at an apparent mass of $1/2(NaI)_n^{+}$. $(NaI)_{13}^{++}$ for example, should appear between $(NaI)_6^{+}$ and $(NaI)_7^{+}$. Figure 7, however, shows that the low mass range of the NaI spectrum is free of these peaks. Only if n exceeds a critical value i.e n=20, doubly charged NaI clusters are detected. The two positive charges generated by electron bombardment are likely to move to opposite sides of the cluster which then explodes into singly charged fragments as long as the Coulomb repulsion energy is greater than the binding energy.

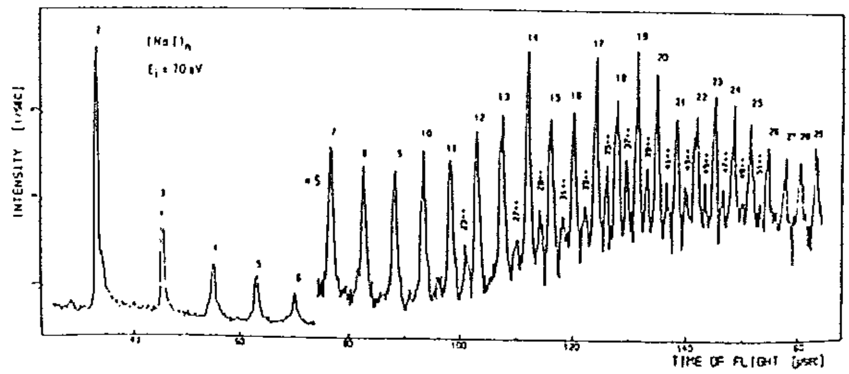


Fig. 7. Mass spectrum of NaI clusters.

The stable configurations of several doubly charged clusters are shown in figure 8. The total binding energy, referenced to ions at infinity. is also indicated for each configuration. For the smallest clusters, the excess Na$^+$ ions are singly coordinated. Such clusters are relatively unstable. The excess ions are easily removed. An exception is Na$_8$Cl$_6^{++}$ which has a highly symmetric configuration for which the excess ions have co-ordination number three. However, the cluster is too small and compact to contain so much excess charge. It has less binding energy than the rectangular configuration which again has only singly coordinated Na$^+$ ions. Starting with the cluster Na$_{10}$Cl$_8^{++}$, the most stable often contains multiply coordinated Na$^+$ ions[3].

they provide microscopic views of such problems as metal insulator transition and the structure of defects in ionic crystals.

Landman, Scharf, and Jortner investigated the properties of an electron interacting with a cluster consisting of n Na^+ and m Cl^- ions[25]. They predicted that the electron could exist in the cluster in one of several situations, depending on the structure of the cluster. It could localize about a specific Na^+ ion or occupy a vacant lattice site as though it were a Cl^- ion, much like an F centre in the bulk crystal. Finally, if there is no favourable site for the electron to localize, it would be delocalized throughout the cluster or at its surface as conduction electron.

Various experiments[26-28] are in agreement with these theoretical predictions.

Recent ultraviolet photoelectron spectroscopy (UPS) studies of $(KI)_n^-$, $K(KI)_n^-$, $K_2(KI)_n^-$ (n up to 13) has suggested the possible existence of electron spin pairs in some of these cluster anions[28].

More recently, Bloomfield and Xia have studied the UPS spectra of sodium chloride cluster anions $(NaCl)_nNa^-$ (n=1-21) which contain two excess electrons[30]. They observed three different modes of accommodating the two electrons. Their evidence suggests that, in some clusters, the electrons form spin pairs that either occupy a single anion vacancy as F' colour centre or localize on a Na^+ cation to form a Na^- anion. In other clusters, the two electrons separately occupy a pair of anion vacancies as a double F colour centre.

The energetics and structure of multiple excess electrons in halogen-deficient Na_nF_m clusters have been studied starting at the stoichiometric ionic limit Na_nF_n and ending with a pure metallic cluster Na_n (for n=2, 3, 4, and partially for n=14)[31]. The results exhibit structural transition upon metallization, ionization potential and F-centre formation energy odd-even oscillation in n-m, and excess metal face segregation for the larger systems.

3. METHODOLOGY AND COMPUTATIONAL DETAILS

The stability of a charged alkali halide cluster comes to an end at a lower limit of size when the Coulomb repulsion energy exceeds the binding energy of the cluster. Theoretical computation of the binding energy of such clusters, therefore, enables one to estimate the critical number of atoms which should be present for the charged cluster to be stable.

Because the binding in alkali halides is almost purely ionic, an alkali halide cluster is best viewed as being composed of ions held together by Coulomb forces. Hence the simplest pair potential which describes ionic bonding has the form:

$$V_{ij} = q_i q_j / r_{ij} \text{..........(6)}$$

where V_{ij} is the potential energy between the ions i and j with respective charges q_i and q_j. r_{ij} is the distance between the charges. Then the total energy of a finite cluster of n ions as a function of position takes the form:

$$V(r_1, ..., r_n) = 1/2 \sum_{i=1,j=1,i\neq j}^{n} q_i q_j / r_{ij} \text{..........(7}$$

The major part (90 percent) of the cohesive energy in ionic crystals is due simply to electrostatic Coulomb interactions among the ions considered as fixed point charges. Therefore the simple potential model which is used throughout this work will not be an oversimplification. Actually this simple potential model will not make distinction among the various alkali halides in calculating their critical Coulomb explosion numbers as the following simple manipulation indicates. Equation 7 can be rewritten as:

$$V(r_1, \ldots, r_n) = 1/2a \sum_{i=1,j=1,i\neq j}^{n} q_i q_j / r_{ij}^{*} \ldots\ldots\ldots (8)$$

where

$r_{ij}^{*} = r_{ij}/\mathbf{a}$

a = lattice constant

Because the scaled distance r_{ij}^{*} is the same for all alkali halides which crystallize in the same lattice type, once the summation is evaluated it can be used for all alkali halides by only varying the appropriate lattice constant.

Turbo Pascal 6.0 computer programs were written to carry out the calculations. A brief description of the programs is given as follows:

Born 501: This program generates a start cell in crystallographic coordinates. The number of ions in the start cell can be varied as required. In crystallographic notation, the length of the unit cell is considered as unity. The position of each ion in the cluster is described by a fraction or multiple of this distance. Most alkali halides crystallize in the NaCl structure. In figure 9, a unit cell of this structure is shown. The Bravais lattice is face centred cubic; the basis consists of one Na atom and one Cl atom separated by one-half of the body diagonal of a unit cube.

There are four units of NaCl in each unit cube, with atoms in the crystallographic positions:

Cl:	0,0,0 ;	1/2,1/2,0 ;	1/2,0,1/2 ;	0,1/2,1/2 .
Na:	1/2,1/2,1/2;	0,0,1/2 ;	0,1/2,0 ;	1/2,0,0 .

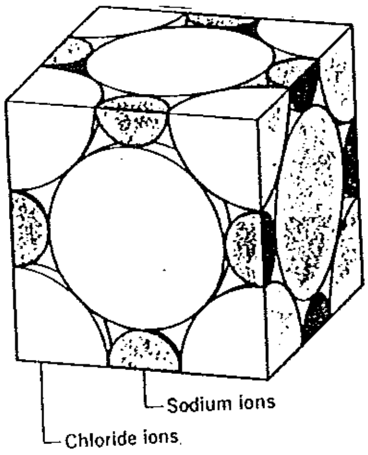


Fig. 9. Unit cell of the NaCl crystal structure.

BORN 502: This program multiplies the start cell according to the relation $N = 8xm^3$. N is the number of ions in the larger cluster and m, a multiplication factor.

BORN 503: In the crystallographic notation, ionic space coordinates were defined by crystallographic axes of the NaCl structure. Born 503 transforms the crystallographic coordinates of each ion into physical coordinates. This is effected by multiplying each coordinate by the appropriate lattice constant. Therefore, once a cluster is generated in crystallographic coordinates, the same cluster can be used for all alkali halides which crystallize in the same crystal structure. All the lattice constants necessary for the calculation are collected from a recent literature[32].

Table 2. Lattice constants of alkali halides in Angstroms.

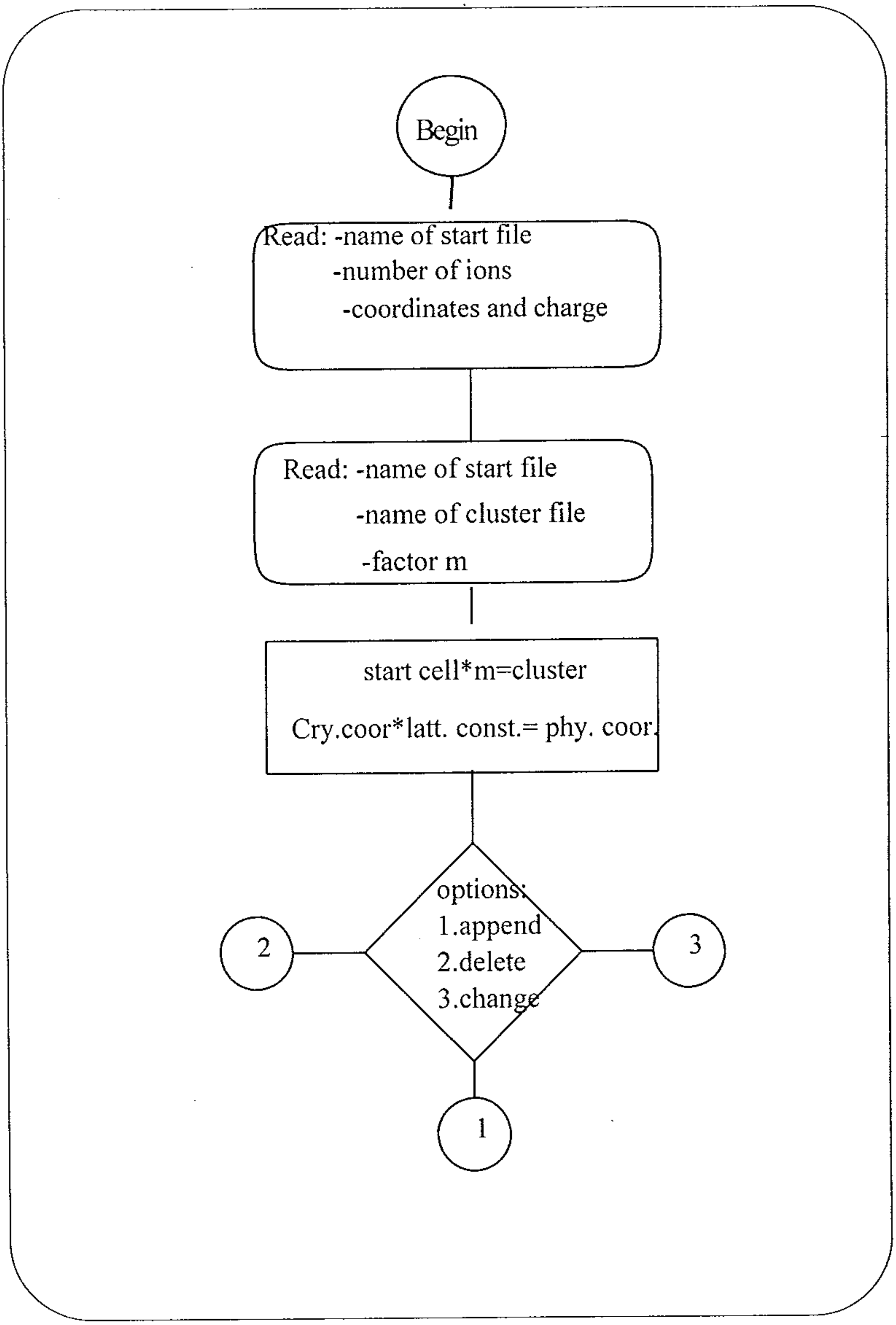
Alkali Halide	Lattice Constant	Alkali Halide	Lattice Constant
LiF	4.0270	KF	5.3470
LiCl	5.1396	KCl	6.2931
LiBr	5.5013	KBr	6.5966
LiI	6.0000	KI	7.0655
NaF	4.6400	RbF	5.6516
NaCl	5.6402	RbCl	6.5810
NaBr	5.9772	RbBr	6.8890
NaI	6.4730	RbI	7.3420

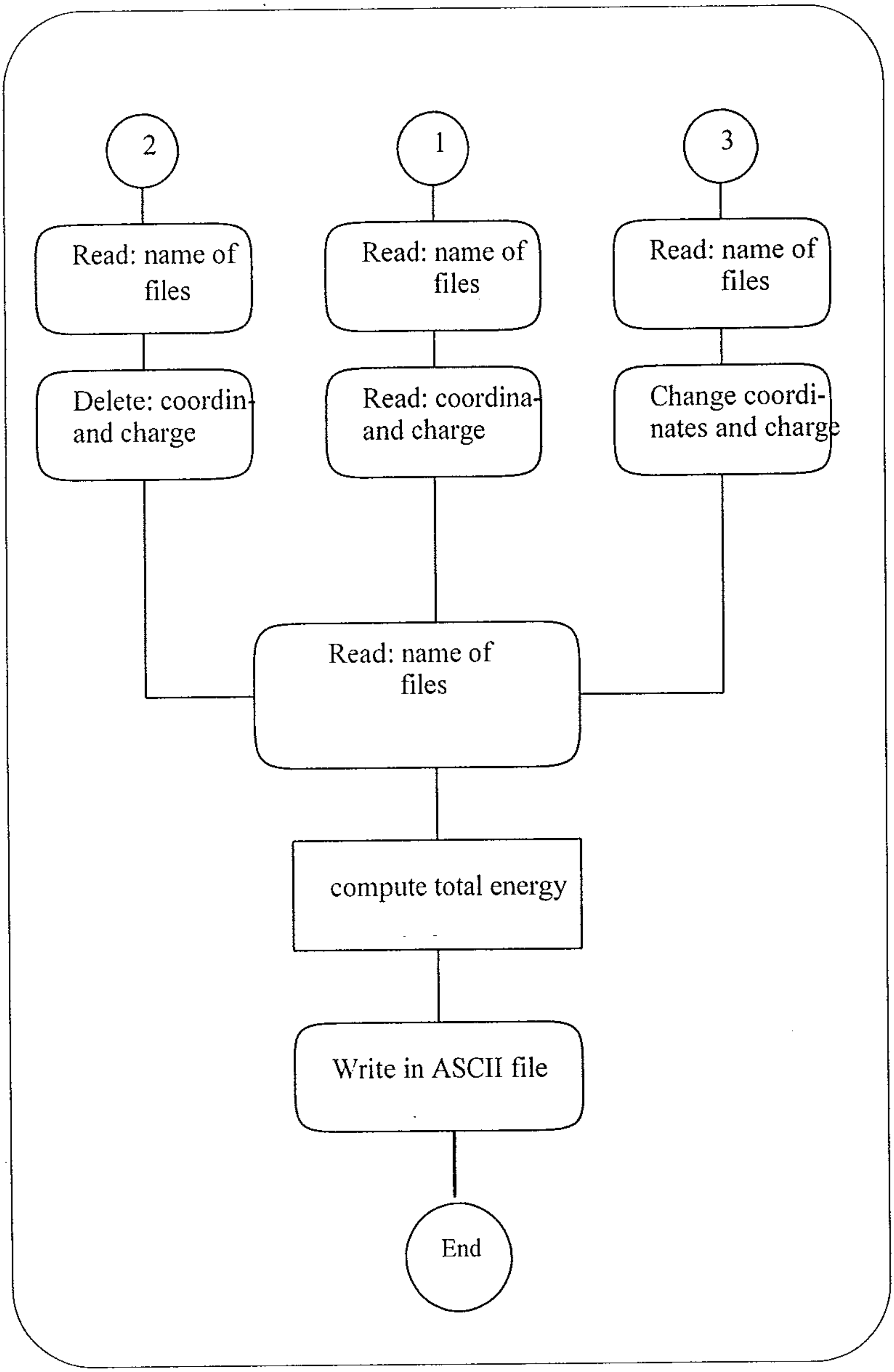
BORN 504: This is a program used to modify the positions or charges of ions in a given cluster. This same program has other options. It delets or appends an ion or group of ions.

BORN 505: Born 505 calculates the coulombic interactions of ions i and j first by establishing the distance between them. In physical coordinates, this distance is simply the square root of the sum of the squares of the coordinate differences. The coulombic contribution for each i-j pair is calculated according to the appropriate charges of the i and j ions. A running summation is made of all the interactions, resulting in a total coulombic energy for the cluster.

BORN 506: In some occasions, viewing the contents of a file is necessary. Born 506 makes it possible.

Generalized flow chart of the programs is given below. The flow chart is merely summary of the foregoing discussions using programming symbolism to show the flow of information in the programs. Flow charting is usually required at the initial stages of program development. Therefore a detailed and more sophisticated flow chart is omitted as it gives no additional information in view of the complete program list in Appendix B.


Begin
Read: -name of start file
-number of ions
-coordinates and charge
Read: -name of start file
-name of cluster file
-factor m
start cell*m=cluster
Cry.coor*latt. const.= phy. coor.
options:
1.append
2.delete
3.change
2
3
1


2
1
3
Read: name of files
Read: name of files
Read: name of files
Delete: coordin- and charge
Read: coordina- and charge
Change coordi- nates and charge
Read: name of files
compute total energy
Write in ASCII file
End

4. RESULTS AND DISCUSSION

4.1 Effect of Sign of Additional Charge

A neutral alkali halide cluster can be made charged either by removing from or adding electrons to it. Removal of electrons is most likely to occur from specific halide ions and there is increased tendency for additional electrons to localize around specific alkali metal ions[33]. This assumption allows a comparison of energies of positively and negatively charged clusters. Two equally but oppositely charged alkali halide clusters have the same critical Coulomb explosion number provided that they share the same geometry.

As an illustration, a 4x4x4 NaCl cluster is considered. This is a symmetric cube in which four corners are occupied by sodium corners and the rest four by chloride ions. All these eight sites are equivalent. If an electron is put at one of the sodium corners, the cluster becomes negatively charged, $(NaCl)_{32}^{-}$. On the other hand, if and electron is removed from one of the chloride corners, the cluster will be positively charged. The energy of these two oppositely charged clusters turns out to be the same, -7.1497×10^{-7} J/cluster. Because the energy of the neutral cluster is affected in the same manner in both cases we conclude that the these two clusters have the same critical Coulomb explosion numbers.

However the above conclusion must be taken with care. It works only for those oppositely charged alkali halide clsuters which have the same geometry. Moreover the single atom positions which are involved in accomodating the additional charge must be equivalent.

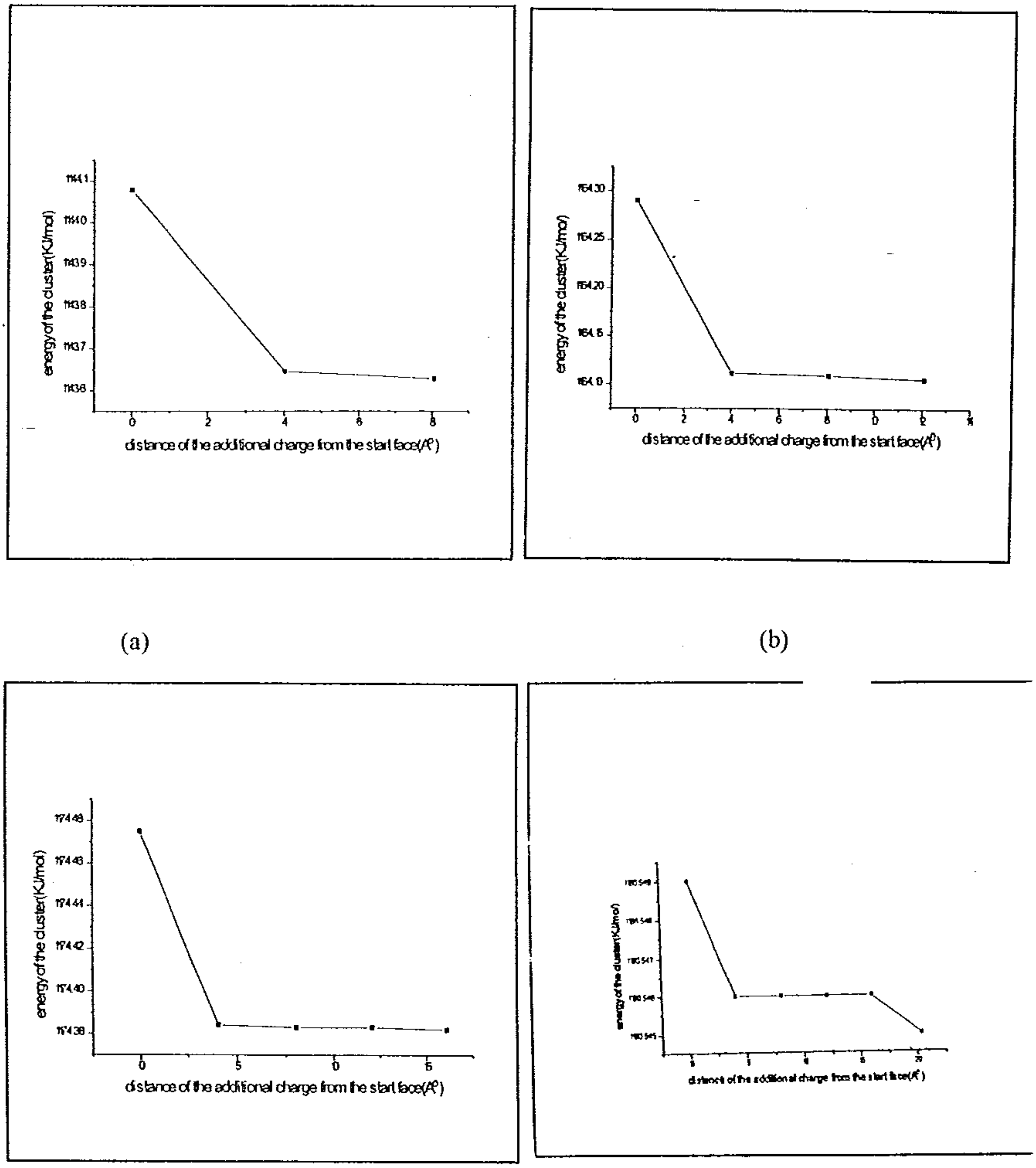
4.2. Effect of Position of Additional Charge

In a charged alkali halide particle, additional charges assume positions which minimize the total energy of the cluster. Thus, prior to calculating the critical Coulomb explosion numbers of a cluster a qualitative search for additional charge positions leading to energy minima have been made. In this respect cubic kxkxk clusters show different behaviours for even and odd k values. Hence, they are considered separately.

4.2.1 Cubic kxkxk Clusters Having Even k Values

First, an additional negative charge was put on a specific metal ion positioned at the centre of one face of a symmetric nxnxn cube(k=4,6,8 and 10) and then the charge was moved, in the calculation, progressively to the opposite face. Plots of the negative of energies of the cluster as a function of distance of the additional charge from the start face are shown for LiF clusters in figure 10.

An important conclusion which can be drawn from these results is that, an additional charge prefers the face of a cluster to its inside. Moreover, as the cluster size increases, the additional charge will not make distinction among the inside ions as its location at each of them will result in almost the same energy. In all the clusters, the first and the second data points refer to additionlal charge positions on the face of the cluster and the next immidiate single atom positions inside the cluster respectively. The slope of these two conscutive data points can roughly be taken as a measure of the relative ease of



(a) (b)

(c) (d)

Fig. 10. Energies of (a) 4x4x4, (b) 6x6x6, (c) 8x8x8 and (d) 10x10x1l charged LiF cluster.

introduction of the additional charge inside the clusters. These slopes are in table 3 for clusters of different sizes.

Table 3. Clusters of different sizes.

cluster	number of ions	slope
6x6x6	216	-0.1075
8x8x8	512	-0.0445
10x10x10	1000	-0.0226
12x12x12	1728	- 0.0007

As the cluster size increases, it becomes easier to introduce additional charges inside clusters. For smaller clusters this is a difficult task as it requires larger energy.

Next, We had to determine the positions of choice of the additional charge on a face. Therefore, the additional charge was moved diagonally from one corner of a face to the opposite. Calculations of the energies of clusters of various size(k=4,6,8,10 and 12) have been carried out. All show similar trend. The energy falls and then rises symmetrically as the charge moves from one corner to the opposite on the same face. A plot of the negative of energy of a cluster as a function of the distance of the additional charge from the start corner is shown in figure 11 for a 10x10x10 KBr cluster. Clearly, those positions towards the corner are favourable sites, the corner being the best. There is an abrupt change in energy of the charged cluster when the additional charge is put at a corner and at single atom position just beside the corner on a face diagonal. This shows that corners are very much favoured in comparison with any other positions on the face. Two additional charge positions on a face diagonal which have the same coordination numbers may result in different energies because the total energy of the cluster is determined by the average coordination. This shows that ions which are far away from the additional charge position have effect on the energy of the cluster.

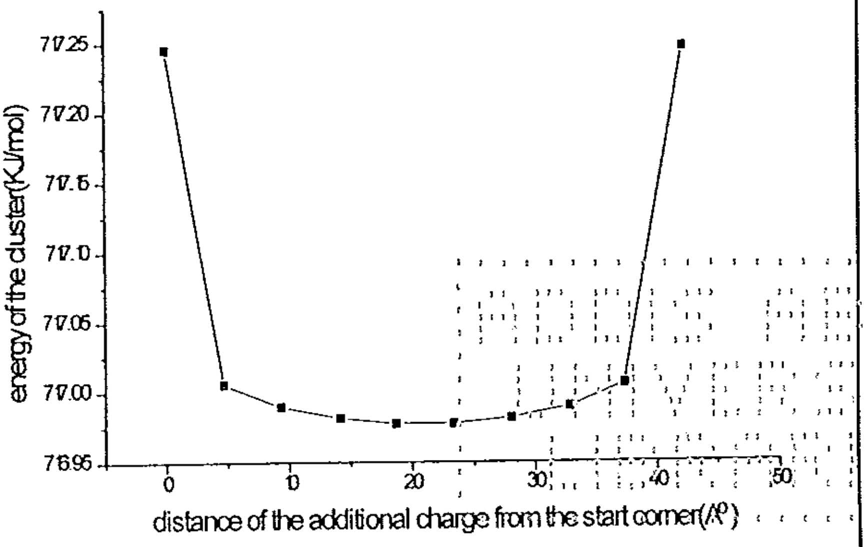
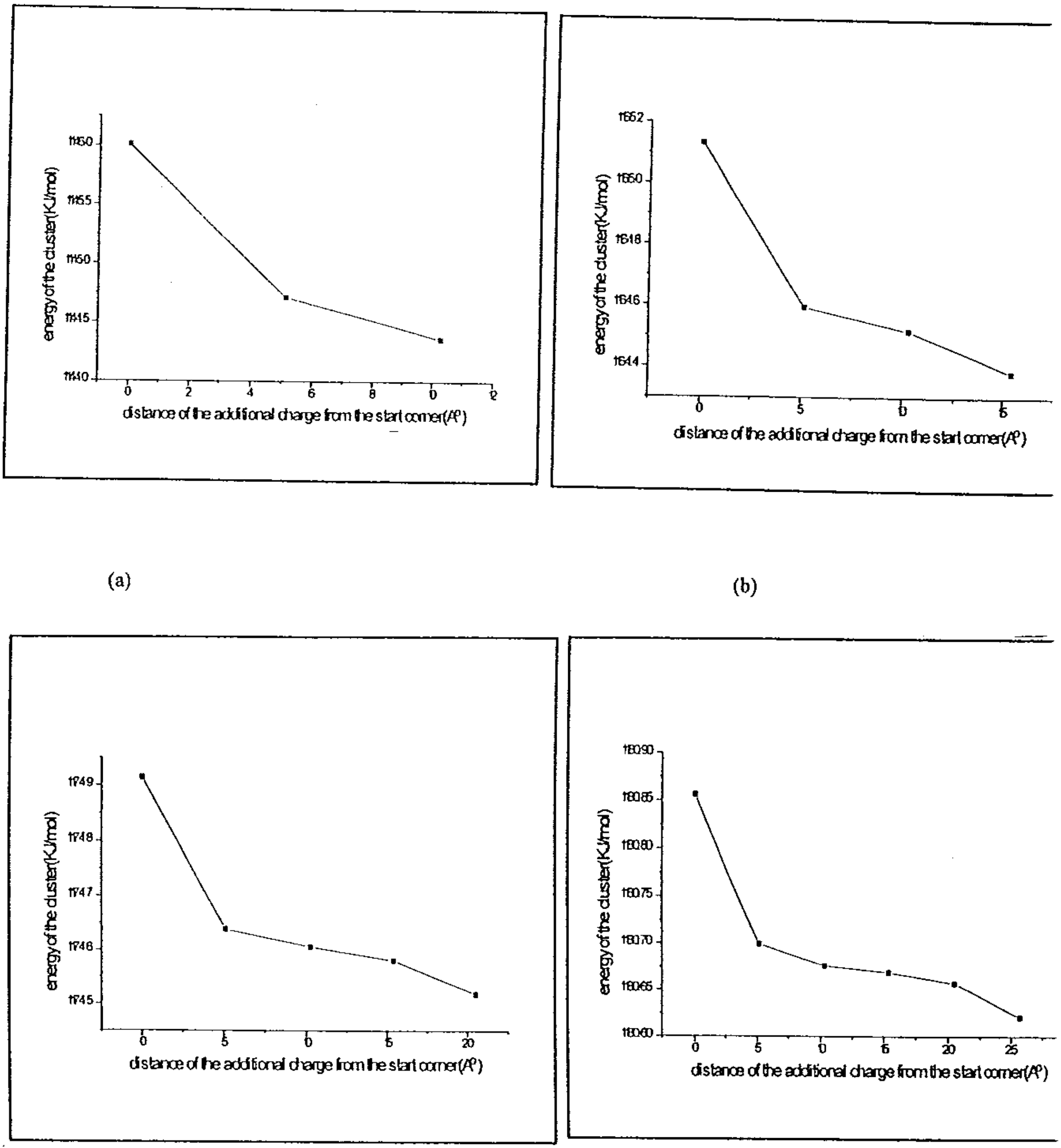


Fig. 11. A 10x10x10 charged KBr cluster.

The additional charge has also been moved along the edges of symmetric cubes of various size. The energy of the clusters decreases in magnitude as the additional charge goes further from the first corner. This is graphically shown for LiCl clusters of different size in Fig.12. Negative of the real energy value is plotted to simplify matters.



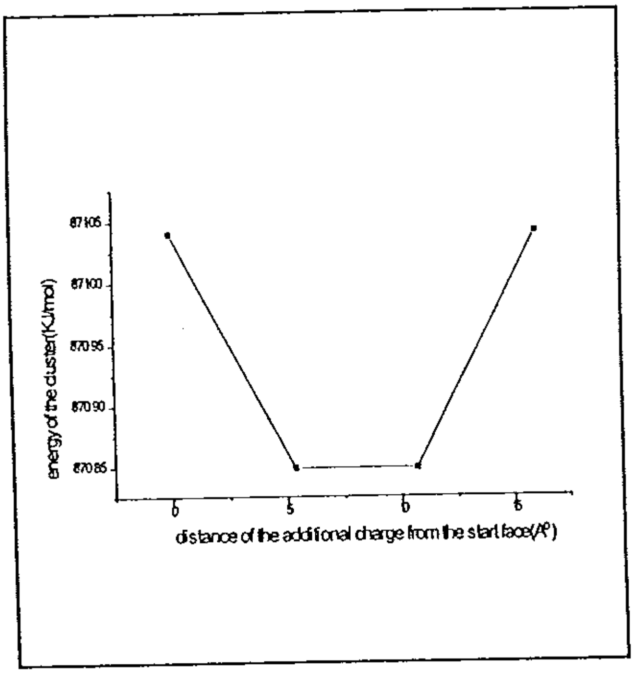
(a) (b)

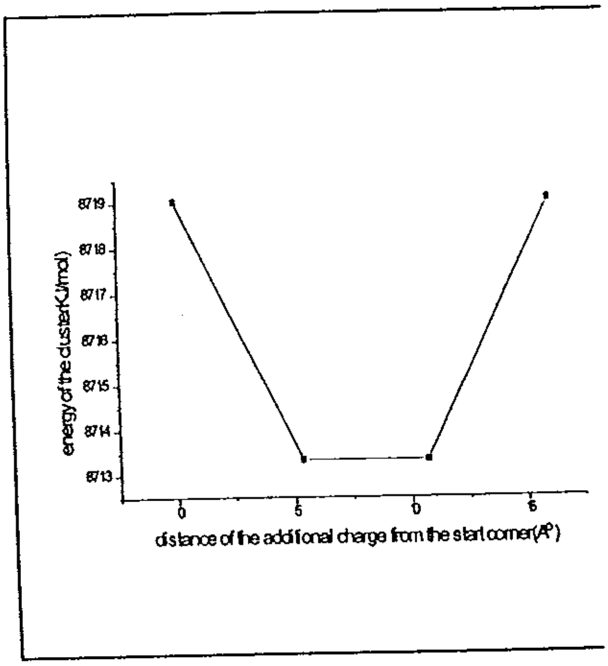
(c) (d)

Fig.12. energies of (a) 6x6x6 (b) 8x8x8 and (c) 10x10x10 and (d) 12x12x12 Charged LiCl clusters.

4.2.2 Cubic kxkxk Clusters Having Odd k Values

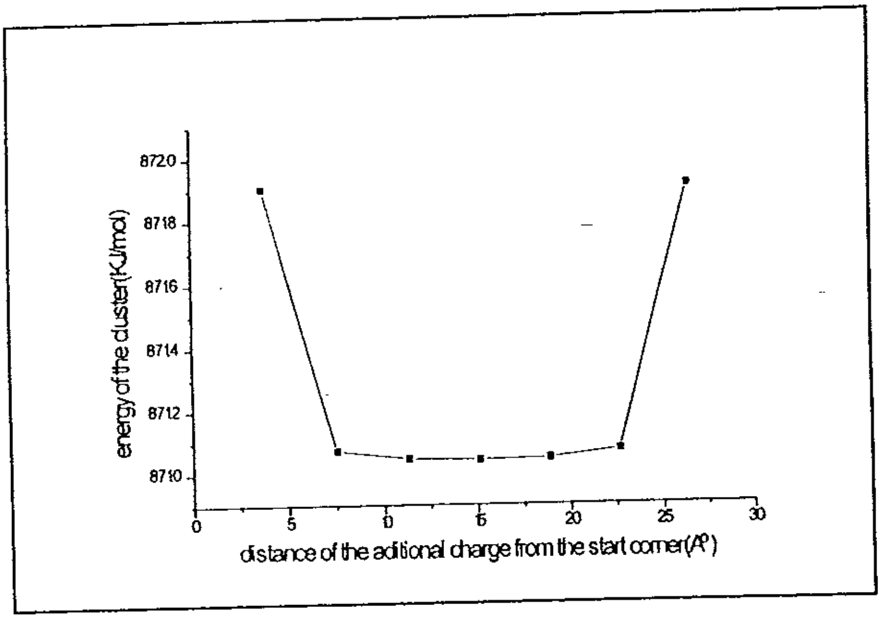
In contrast to cubic clusters having even k values, those with odd k values show different behaviour especially when the additional charge is moved between two parallel faces and along an edge. This is due to the fact that in the latter, all eight corners are occupied by identical ions and therefore there is a plane of symmetry passing between two opposite faces and parallel to both. Therefore in all the three cases i.e as the additional charge moves on a face diagonal, along an edge and between two parallel faces, the energy of the cluster(magnitude) falls and then rises in a symmetrical fashion. The case of a 7x7x7 KF cluster is shown in figure 13.





(a)

(b)



(c)

Fig.13. Energies of charged KF clusters. Charge moves (a)between parallel faces

(b) along an edge (c) on a face diagonal

The foregoing results show that additional charges localize at positions in cubic clusters in the decreasing order of preference: corner > edge > face > body inside. Detailed quantitative investigation of these results is not important for our purpose. However it is very clear from the curves that corner positions are favoured over the face or body inside positions by many factors.

4.2.3. Interaction Between Charges

The interaction between two additional charges has been studied. When two charges are introduced into a cluster, both assume corner positions as the foregoing results witness. Variation of the cluster shape gives ideas about the interaction between the charges. As table 4 shows a cluster composed of 64 ions can have different shapes of which three are indicated. As the distance between the additional charges increases, so does the ease with which they are introduced.

Table 4. $(RbI)_{32}^{-2}$ clusters of different size

Cluster shape	Energy difference between neutral and charged cluster(eV)
4x4x4	11.864647
2x8x4	11.697148
2x2x16	11.590107

4.3. Stability Ranges

Having examined the effects of the sign and the position of the additional charges, the next task was to determine the stability ranges. The procedure is simple. The required additional charges are introduced into a cluster of arbitrary size according to the general guide lines in the preceding sections. If the total energy of the charged cluster is positive with respect to ions at infinity, the size of the cluster is reduced until the energy becomes zero. In many cases, the energy will not be exactly zero. So, one has to look for the size at which the total energy changes sign. Table 5 shows the critical Coulomb explosion sizes for charged alkali halides, $(MX)_n$. As the values in the last column of Appendix A reveal, those alkali halides with larger cation and anion size have lower tendency to undergo Coulomb explosion. However, this is is compensated by the fact that they have lower total energies in their neutral states.

Table 5. critical coulomb explosion numbers, n* of multiply charged alkali halide particles.

additional charge	-2	-3	-4	-5	-6	-7	-8	-9	-10
n*	3	4	6	9	11	13	16	18	21

Clearly, the cluster size increases with increasing number of additional charges. The irregularity in critical size increment per additional charge is probably due to differences in the structures of the clusters. That is to say, some clusters have higher capability to hold charges than others because of their structures. The critical Coulomb explosion number, n* of these clusters is plotted against charge in figure 14. A linear regression fit of these data points gives a slope of -2.3 with a correlation coefficient of 0.996. Therefore, the simple relation between the critical Coulomb explosion number and additional charge can be approximated to the equation:

$$n^* = -2.3z - 2.578$$

where z is the additional charge.

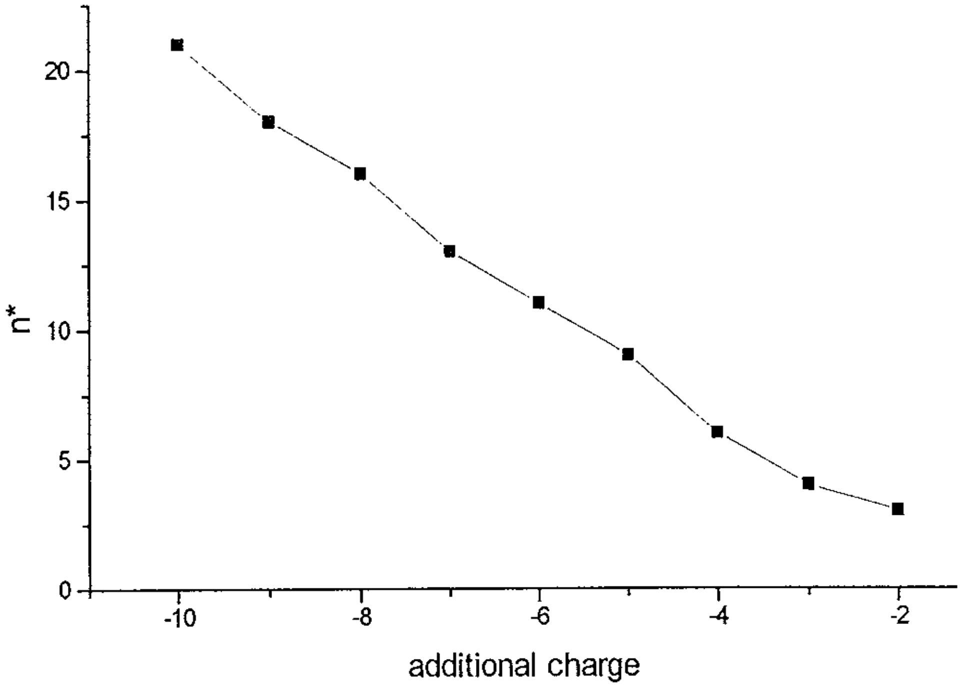


Fig. 14 Plot of critical Coulomb explosion numbers of chaged alkali halide clusters as a function of charge of the clusters.

4.4. Stable Geometries

It has been mentioned in section 2.1 that we must rely on total energy calculation for a knowledge of the stable geometries of small clusters. A number of such theoretical studies which make use of different potential models have been reported[3,16,17]. Using a simpler potential model, i.e., equation 6, than those used in previous works, We have calculated the binding energies of neutral $(NaCl)_n$ clusters where n ranges from 2 to 12. Our results are shown in figure 15. Notice that for each cluster size more than one stable configurations are shown. An enhanced stability of clusters which can be represented by cuboids, i.e., small fractions of the rock salt lattice has been observed. Stacks of hexagonal rings are also found to be favoured structures. The difference in total energy of clusters is generally less than 10 percent compared with other results which employ more sophisticated potential models[3,16]. This is to be expected since short range repulsion and polarisation terms are neglected in our model. In predicting stable geometries, the most important thing is order of stability of the various geometries proposed for a cluster of a given size. In this regard, our simple model agrees well with the predictions of the refined models[3,16].

5. CONCLUSION

The critical Coulomb explosion numbers of charged alkali halide clusters were calculated. The charge of the clusters ranges in magnitude from 2 to 10. It has been found that the critical Coulomb explosion number increases with increasing charge of the clusters. The critical Coulomb explosion number is linearly related with the additional charge with a good correlation. The influence of the sign and position of the charges was assessed. Equally but oppositively charged clusters exhibit identical Coulomb explosion number on the assumption that they share the same geometry. Charges localize at single atom positions of cubic clusters in the decreasing order of preference: corner>edge>face>body inside.

The potential model used in this work is a very simple one.No any geometry optimization has been done. Therefore, care must be taken in considering these predictions. However we believe that this work will serve as a starting point for more refined treatments. The binding energies of the most tightly bound isomers of $(NaCl)_n$, n=2-12, were calculated using a very simple potential model which considers only the electrostatic Coulomb interactions. The stability order of the isomers of a given cluster follows more or less the same order as the predictions of the other sophisticated potential models.

```
BORN 507 Conversion of a Crystallographic to Physical Files and
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2 additional negative charges in a cluster of 4 ions.
Perfect Cluster : naz.cry
Defect Cluster  : nazn.cry
ASCII-File      : nazn.asc
   Perfect Cluster          Defect Cluster              Difference
  E/Cluster  E/mol        E/Cluster  E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   1.99426E-0018       600477-8.10207E-0019   -243955-2.80447E-0018-17.503968
NaF   1.73079E-0018       521146-7.03169E-0019   -211726-2.43396E-0018-15.191482
KF    1.50194E-0018       452238-6.10193E-0019   -183731-2.11214E-0018-13.182809
RbF   1.42099E-0018       427865-5.77306E-0019   -173828-1.99830E-0018-12.472305
LiCl  1.56255E-0018       470488-6.34817E-0019   -191145-2.19737E-0018-13.714779
NaCl  1.42386E-0018       428729-5.78473E-0019   -174180-2.00234E-0018-12.497514
KCl   1.27614E-0018       384249-5.18457E-0019   -156109-1.79460E-0018-11.200915
RbCl  1.22031E-0018       367439-4.95776E-0019   -149279-1.71609E-0018-10.710907
LiBr  1.45982E-0018       439554-5.93079E-0019   -178577-2.05289E-0018-12.813058
NaBr  1.34359E-0018       404557-5.45858E-0019   -164359-1.88944E-0018-11.792893
KBr   1.21743E-0018       366571-4.94604E-0019   -148926-1.71203E-0018-10.685577
RbBr  1.16575E-0018       351012-4.73611E-0019   -142605-1.63937E-0018-10.232033
LiI   1.33848E-0018       403020-5.43784E-0019   -163735-1.88226E-0018-11.748080
NaI   1.24067E-0018       373570-5.04048E-0019   -151770-1.74472E-0018-10.889615
KI    1.13663E-0018       342243-4.61779E-0019   -139043-1.59841E-0018 -9.976432
RbI   1.09383E-0018       329354-4.44389E-0019   -133807-1.53822E-0018 -9.600719
```

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BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

2 additional negative charges in a cluster of 6 ions.
Perfect Cluster : nap.cry
Defect Cluster  : nanp.cry
ASCII-File      : nanp.asc
   Perfect Cluster          Defect Cluster            Difference
  E/Cluster   E/mol       E/Cluster  E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   3.99819E-0018    802576 5.22522E-0019    104888-3.47566E-0018-21.693219
NaF   3.46998E-0018    696546 4.53490E-0019     91031-3.01649E-0018-18.827283
KF    3.01116E-0018    604446 3.93528E-0019     78995-2.61764E-0018-16.337871
RbF   2.84887E-0018    571869 3.72318E-0019     74737-2.47655E-0018-15.457321
LiCl  3.13267E-0018    628837 4.09408E-0019     82183-2.72327E-0018-16.997158
NaCl  2.85463E-0018    573024 3.73071E-0019     74888-2.48156E-0018-15.488563
KCl   2.55847E-0018    513574 3.34365E-0019     67119-2.22410E-0018-13.881647
RbCl  2.44654E-0018    491107 3.19738E-0019     64183-2.12680E-0018-13.274365
LiBr  2.92671E-0018    587493 3.82490E-0019     76779-2.54422E-0018-15.879627
NaBr  2.69368E-0018    540717 3.52037E-0019     70666-2.34165E-0018-14.615304
KBr   2.44076E-0018    489945 3.18982E-0019     64031-2.12177E-0018-13.242973
RbBr  2.33716E-0018    469150 3.05443E-0019     61313-2.03172E-0018-12.680882
LiI   2.68345E-0018    538662 3.50699E-0019     70398-2.33275E-0018-14.559766
NaI   2.48736E-0018    499301 3.25073E-0019     65253-2.16229E-0018-13.495843
KI    2.27878E-0018    457430 2.97813E-0019     59781-1.98096E-0018-12.364107
RbI   2.19296E-0018    440203 2.86597E-0019     57530-1.90636E-0018-11.898474
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BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

3 additional negative charges in a cluster of 8 ions.
Perfect Cluster : NA2.CRY
Defect Cluster  : NA3.CRY
ASCII-File      : NA2.ASC
   Perfect Cluster        Defect Cluster              Difference
  E/Cluster   E/mol      E/Cluster   E/mol      E/Cluster[J]  E/Cluster[eV]

LiF   6.67331E-0018    1004675-7.62293E-0019    -114764-7.43560E-0018-46.409018
NaF   5.79168E-0018     871945-6.61585E-0019     -99602-6.45327E-0018-40.277827
KF    5.02589E-0018     756653-5.74108E-0019     -86433-5.59999E-0018-34.952145
RbF   4.75501E-0018     715873-5.43166E-0019     -81774-5.29818E-0018-33.068355
LiCl  5.22870E-0018     787187-5.97275E-0019     -89921-5.82597E-0018-36.362580
NaCl  4.76462E-0018     717320-5.44264E-0019     -81940-5.30888E-0018-33.135193
KCl   4.27030E-0018     642899-4.87797E-0019     -73438-4.75810E-0018-29.697465
RbCl  4.08348E-0018     614774-4.66457E-0019     -70226-4.54994E-0018-28.398286
LiBr  4.88492E-0018     735431-5.58005E-0019     -84008-5.44293E-0018-33.971810
NaBr  4.49599E-0018     676876-5.13578E-0019     -77320-5.00956E-0018-31.267001
KBr   4.07383E-0018     613320-4.65354E-0019     -70060-4.53918E-0018-28.331128
RbBr  3.90092E-0018     587288-4.45603E-0019     -67086-4.34652E-0018-27.128628
LiI   4.47890E-0018     674304-5.11626E-0019     -77026-4.99053E-0018-31.148186
NaI   4.15162E-0018     625031-4.74240E-0019     -71397-4.62586E-0018-28.872102
KI    3.80347E-0018     572617-4.34471E-0019     -65410-4.23794E-0018-26.450940
RbI   3.66023E-0018     551052-4.18109E-0019     -62947-4.07834E-0018-25.454797
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BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

3 additional negative charges in a cluster of 10 ions.
Perfect Cluster : nas.cry
Defect Cluster  : nasn.cry
ASCII-File      : nasn.asc
   Perfect Cluster          Defect Cluster              Difference
  E/Cluster   E/mol       E/Cluster   E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   7.49283E-0018       902444 1.03931E-0018     125175-6.45352E-0018-40.279385
NaF   6.50293E-0018       783220 9.02003E-0019     108638-5.60093E-0018-34.957992
KF    5.64309E-0018       679660 7.82737E-0019      94274-4.86036E-0018-30.335718
RbF   5.33895E-0018       643029 7.40551E-0019      89193-4.59840E-0018-28.700737
LiCl  5.87081E-0018       707086 8.14323E-0019      98078-5.05649E-0018-31.559865
NaCl  5.34974E-0018       644328 7.42047E-0019      89373-4.60769E-0018-28.758747
KCl   4.79471E-0018       577480 6.65061E-0019      80101-4.12965E-0018-25.775068
RbCl  4.58496E-0018       552217 6.35967E-0019      76596-3.94899E-0018-24.647483
LiBr  5.48482E-0018       660597 7.60783E-0019      91629-4.72403E-0018-29.484864
NaBr  5.04812E-0018       608000 7.00210E-0019      84334-4.34791E-0018-27.137302
KBr   4.57412E-0018       550911 6.34463E-0019      76415-3.93965E-0018-24.589195
RbBr  4.37997E-0018       527528 6.07533E-0019      73172-3.77244E-0018-23.545519
LiI   5.02894E-0018       605690 6.97549E-0019      84014-4.33139E-0018-27.034180
NaI   4.66146E-0018       561431 6.46578E-0019      77874-4.01488E-0018-25.058718
KI    4.27056E-0018       514350 5.92357E-0019      71344-3.67820E-0018-22.957340
RbI   4.10973E-0018       494980 5.70049E-0019      68657-3.53968E-0018-22.092765
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BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

4 additional negative charges in a cluster of 10 ions.
Perfect Cluster : NA2.CRY
Defect Cluster  : NA5.CRY
ASCII-File      : NA5.ASC
   Perfect Cluster            Defect Cluster              Difference
  E/Cluster  E/mol         E/Cluster  E/mol       E/Cluster[J]  E/Cluster[eV]

LiF   7.49283E-0018      902444-2.27758E-0018    -274314-9.77040E-0018-60.981600
NaF   6.50293E-0018      783220-1.97668E-0018    -238074-8.47962E-0018-52.925195
KF    5.64309E-0018      679660-1.71532E-0018    -206595-7.35841E-0018-45.927231
RbF   5.33895E-0018      643029-1.62287E-0018    -195460-6.96182E-0018-43.451926
LiCl  5.87081E-0018      707086-1.78454E-0018    -214931-7.65535E-0018-47.780548
NaCl  5.34974E-0018      644328-1.62615E-0018    -195855-6.97589E-0018-43.539751
KCl   4.79471E-0018      577480-1.45744E-0018    -175535-6.25215E-0018-39.022565
RbCl  4.58496E-0018      552217-1.39368E-0018    -167856-5.97864E-0018-37.315439
LiBr  5.48482E-0018      660597-1.66721E-0018    -200800-7.15202E-0018-44.639068
NaBr  5.04812E-0018      608000-1.53447E-0018    -184813-6.58258E-0018-41.084940
KBr   4.57412E-0018      550911-1.39038E-0018    -167459-5.96450E-0018-37.227194
RbBr  4.37997E-0018      527528-1.33137E-0018    -160351-5.71134E-0018-35.647105
LiI   5.02894E-0018      605690-1.52863E-0018    -184110-6.55757E-0018-40.928817
NaI   4.66146E-0018      561431-1.41693E-0018    -170657-6.07839E-0018-37.938036
KI    4.27056E-0018      514350-1.29811E-0018    -156346-5.56867E-0018-34.756621
RbI   4.10973E-0018      494980-1.24922E-0018    -150458-5.35895E-0018-33.447685
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

4 additional charges in a cluster of 12 ions.
Perfect Cluster : bf.cry
Defect Cluster  : bf1.cry
ASCII-File      : bf1.asc
   Perfect Cluster          Defect Cluster            Difference
  E/Cluster   E/mol       E/Cluster   E/mol     E/Cluster[J]   E/Cluster[eV]

LiF   8.98354E-0018      901656 8.73461E-0021       877-8.97481E-0018-56.015920
NaF   7.79671E-0018      782536 7.58067E-0021       761-7.78913E-0018-48.615541
KF    6.76580E-0018      679066 6.57832E-0021       660-6.75922E-0018-42.187416
RbF   6.40115E-0018      642467 6.22378E-0021       625-6.39492E-0018-39.913672
LiCl  7.03882E-0018      706469 6.84378E-0021       687-7.03198E-0018-43.889818
NaCl  6.41409E-0018      643766 6.23636E-0021       626-6.40785E-0018-39.994346
KCl   5.74863E-0018      576976 5.58934E-0021       561-5.74304E-0018-35.844991
RbCl  5.49715E-0018      551735 5.34483E-0021       536-5.49180E-0018-34.276874
LiBr  6.57603E-0018      660020 6.39381E-0021       642-6.56964E-0018-41.004146
NaBr  6.05245E-0018      607470 5.88474E-0021       591-6.04657E-0018-37.739428
KBr   5.48415E-0018      550430 5.33219E-0021       535-5.47882E-0018-34.195815
RbBr  5.25138E-0018      527068 5.10586E-0021       512-5.24627E-0018-32.744391
LiI   6.02946E-0018      605161 5.86238E-0021       588-6.02359E-0018-37.596018
NaI   5.58887E-0018      560941 5.43400E-0021       545-5.58343E-0018-34.848773
KI    5.12019E-0018      513901 4.97832E-0021       500-5.11522E-0018-31.926419
RbI   4.92737E-0018      494548 4.79083E-0021       481-4.92258E-0018-30.724068
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```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

5 additional charges in a cluster of 16 ions.
Perfect Cluster : nax.cry
Defect Cluster  : naxn.cry
ASCII-File      : naxn.asc
   Perfect Cluster        Defect Cluster            Difference
  E/Cluster   E/mol      E/Cluster  E/mol    E/Cluster[J]  E/Cluster[eV]

LiF   1.39786E-0017   1052245-2.12604E-0019    -16004-1.41912E-0017-88.573648
NaF   1.21318E-0017    913231-1.84517E-0019    -13890-1.23163E-0017-76.872000
KF    1.05277E-0017    792480-1.60119E-0019    -12053-1.06878E-0017-66.707701
RbF   9.96031E-0018    749769-1.51489E-0019    -11403-1.01118E-0017-63.112407
LiCl  1.09525E-0017    824460-1.66580E-0019    -12539-1.11191E-0017-69.399580
NaCl  9.98044E-0018    751284-1.51795E-0019    -11426-1.01322E-0017-63.239970
KCl   8.94499E-0018    673339-1.36047E-0019    -10241-9.08103E-0018-56.678915
RbCl  8.55367E-0018    643883-1.30095E-0019     -9793-8.68376E-0018-54.199374
LiBr  1.02324E-0017    770253-1.55628E-0019    -11715-1.03881E-0017-64.836689
NaBr  9.41774E-0018    708926-1.43237E-0019    -10782-9.56097E-0018-59.674443
KBr   8.53344E-0018    642360-1.29788E-0019     -9770-8.66323E-0018-54.071200
RbBr  8.17124E-0018    615095-1.24279E-0019     -9355-8.29552E-0018-51.776176
LiI   9.38195E-0018    706232-1.42693E-0019    -10741-9.52464E-0018-59.447680
NaI   8.69638E-0018    654626-1.32266E-0019     -9956-8.82865E-0018-55.103674
KI    7.96712E-0018    599730-1.21174E-0019     -9121-8.08830E-0018-50.482780
RbI   7.66708E-0018    577144-1.16611E-0019     -8778-7.78369E-0018-48.581596
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

5 additional negative charges in a cluster of 18 ions.
Perfect Cluster : na3
Defect Cluster  : na6
ASCII-File      : na6.asc
   Perfect Cluster         Defect Cluster            Difference
  E/Cluster  E/mol       E/Cluster  E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   1.48304E-0017    992329 2.04957E-0018    137140-1.27809E-0017-79.771326
NaF   1.28712E-0017    861231 1.77879E-0018    119022-1.10924E-0017-69.232571
KF    1.11693E-0017    747356 1.54359E-0018    103284-9.62569E-0018-60.078386
RbF   1.05673E-0017    707076 1.46040E-0018     97718-9.10690E-0018-56.840387
LiCl  1.16200E-0017    777514 1.60588E-0018    107452-1.00141E-0017-62.502749
NaCl  1.05887E-0017    708505 1.46335E-0018     97915-9.12531E-0018-56.955273
KCl   9.49011E-0018    634999 1.31153E-0018     87757-8.17857E-0018-51.046246
RbCl  9.07494E-0018    607219 1.25416E-0018     83918-7.82078E-0018-48.813118
LiBr  1.08560E-0017    726394 1.50030E-0018    100388-9.35571E-0018-58.393313
NaBr  9.99166E-0018    668559 1.38085E-0018     92395-8.61082E-0018-53.744083
KBr   9.05348E-0018    605783 1.25119E-0018     83719-7.80229E-0018-48.697682
RbBr  8.66921E-0018    580071 1.19808E-0018     80166-7.47112E-0018-46.630735
LiI   9.95370E-0018    666018 1.37560E-0018     92044-8.57810E-0018-53.539855
NaI   9.22635E-0018    617351 1.27508E-0018     85318-7.95127E-0018-49.627550
KI    8.45265E-0018    565581 1.16816E-0018     78163-7.28449E-0018-45.465874
RbI   8.13432E-0018    544281 1.12416E-0018     75220-7.01016E-0018-43.753627
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

6 additional negative charges in a cluster of 20 ions.
Perfect Cluster : na4.cry
Defect Cluster  : na3.cry
ASCII-File      : naaa6.asc
   Perfect Cluster          Defect Cluster           Difference
  E/Cluster  E/mol        E/Cluster  E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   1.62314E-0017      977460-1.15368E-0018      -69475-1.73850E-0017-108.507985
NaF   1.40870E-0017      848326-1.00126E-0018      -60296-1.50883E-0017-94.172771
KF    1.22244E-0017      736157-8.68871E-0019      -52324-1.30932E-0017-81.720901
RbF   1.15655E-0017      696481-8.22042E-0019      -49504-1.23876E-0017-77.316451
LiCl  1.27177E-0017      765864-9.03933E-0019      -54435-1.36216E-0017-85.018612
NaCl  1.15889E-0017      697889-8.23704E-0019      -49604-1.24126E-0017-77.472724
KCl   1.03866E-0017      625484-7.38246E-0019      -44458-1.11248E-0017-69.435041
RbCl  9.93218E-0018      598121-7.05950E-0019      -42513-1.06381E-0017-66.397456
LiBr  1.18815E-0017      715509-8.44501E-0019      -50856-1.27260E-0017-79.428800
NaBr  1.09355E-0017      658541-7.77263E-0019      -46807-1.17128E-0017-73.104741
KBr   9.90869E-0018      596706-7.04280E-0019      -42412-1.06130E-0017-66.240435
RbBr  9.48812E-0018      571379-6.74387E-0019      -40612-1.01625E-0017-63.428895
LiI   1.08939E-0017      656039-7.74309E-0019      -46629-1.16683E-0017-72.826943
NaI   1.00979E-0017      608100-7.17728E-0019      -43222-1.08156E-0017-67.505277
KI    9.25110E-0018      557106-6.57541E-0019      -39597-9.90864E-0018-61.844407
RbI   8.90271E-0018      536125-6.32778E-0019      -38106-9.53548E-0018-59.515344
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

'/ additional negative charges in a cluster of 24 ions
Perfect Cluster  : ab.cry
Defect Cluster   : ab1.cry
ASCII-File       : ab1.asc
   Perfect Cluster          Defect Cluster              Difference
  E/Cluster  E/mol        E/Cluster  E/mol       E/Cluster[J]  E/Cluster[eV]

LiF    2.11689E-0017    1062336-1.16205E-0018    -58316-2.23310E-0017-139.377918
NaF    1.83723E-0017     921989-1.00853E-0018    -50612-1.93808E-0017-120.964413
KF     1.59430E-0017     800080-8.75177E-0019    -43920-1.68182E-0017-104.970053
RbF    1.50837E-0017     756959-8.28008E-0019    -41553-1.59117E-0017-99.312562
LiCl   1.65864E-0017     832366-9.10493E-0019    -45692-1.74969E-0017-109.205945
NaCl   1.51142E-0017     758489-8.29682E-0019    -41637-1.59439E-0017-99.513293
KCl    1.35461E-0017     679797-7.43603E-0019    -37317-1.42898E-0017-89.188933
RbCl   1.29535E-0017     650057-7.11073E-0019    -35684-1.36646E-0017-85.287171
LiBr   1.54958E-0017     777639-8.50630E-0019    -42688-1.63465E-0017-102.025862
NaBr   1.42621E-0017     715724-7.82903E-0019    -39289-1.50450E-0017-93.902643
KBr    1.29229E-0017     648520-7.09391E-0019    -35600-1.36323E-0017-85.085480
RbBr   1.23744E-0017     620994-6.79281E-0019    -34089-1.30537E-0017-81.474071
LiI    1.42079E-0017     713005-7.79928E-0019    -39140-1.49878E-0017-93.545813
NaI    1.31697E-0017     660903-7.22937E-0019    -36280-1.38926E-0017-86.710161
KI     1.20653E-0017     605481-6.62313E-0019    -33237-1.27276E-0017-79.438805
RbI    1.16109E-0017     582679-6.37370E-0019    -31986-1.22483E-0017-76.447136
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

7 additional charges in a cluster of 26 ions.
Perfect Cluster : ac.cry
Defect Cluster  : ac1.cry
ASCII-File      : ac1.asc
   Perfect Cluster        Defect Cluster             Difference
  E/Cluster   E/mol      E/Cluster  E/mol      E/Cluster[J]  E/Cluster[eV]

LiF   2.20566E-0017  1021740 1.14615E-0018      53093-2.09105E-0017-130.511982
NaF   1.91427E-0017   886755 9.94727E-0019      46079-1.81480E-0017-113.269774
KF    1.66116E-0017   769505 8.63200E-0019      39986-1.57484E-0017-98.292828
RbF   1.57163E-0017   728032 8.16677E-0019      37831-1.48996E-0017-92.995214
LiCl  1.72819E-0017   800557 8.98033E-0019      41600-1.63839E-0017-102.259271
NaCl  1.57480E-0017   729503 8.18328E-0019      37908-1.49297E-0017-93.183176
KCl   1.41142E-0017   653819 7.33427E-0019      33975-1.33808E-0017-83.515557
RbCl  1.34967E-0017   625216 7.01342E-0019      32489-1.27954E-0017-79.861989
LiBr  1.61456E-0017   747922 8.38989E-0019      38865-1.53067E-0017-95.535919
NaBr  1.48601E-0017   688373 7.72190E-0019      35770-1.40880E-0017-87.929423
KBr   1.34648E-0017   623737 6.99683E-0019      32412-1.27651E-0017-79.673127
RbBr  1.28933E-0017   597263 6.69986E-0019      31036-1.22233E-0017-76.291443
LiI   1.48037E-0017   685758 7.69255E-0019      35635-1.40344E-0017-87.595292
NaI   1.37219E-0017   635647 7.13044E-0019      33031-1.30089E-0017-81.194462
KI    1.25712E-0017   582343 6.53249E-0019      30261-1.19180E-0017-74.385641
RbI   1.20978E-0017   560412 6.28648E-0019      29121-1.14692E-0017-71.584275
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

8 additional negative charges in a cluste of 30 ions.
Perfect Cluster : ad.cry
Defect Cluster  : ad1.cry
ASCII-File      : ad1.asc
   Perfect Cluster          Defect Cluster            Difference
  E/Cluster  E/mol         E/Cluster  E/mol      E/Cluster[J]  E/Cluster[eV]

LiF   2.60899E-0017    1047433-1.09400E-0018    -43921-2.71839E-0017-169.667507
NaF   2.26431E-0017     909054-9.49468E-0019    -38118-2.35926E-0017-147.252381
KF    1.96492E-0017     788856-8.23926E-0019    -33078-2.04731E-0017-127.782130
RbF   1.85902E-0017     746340-7.79520E-0019    -31295-1.93697E-0017-120.895153
LiCl  2.04421E-0017     820689-8.57174E-0019    -34413-2.12993E-0017-132.938565
NaCl  1.86277E-0017     747848-7.81095E-0019    -31359-1.94088E-0017-121.139507
KCl   1.66951E-0017     670260-7.00058E-0019    -28105-1.73952E-0017-108.571459
RbCl  1.59648E-0017     640938-6.69432E-0019    -26876-1.66342E-0017-103.821767
LiBr  1.90981E-0017     766730-8.00817E-0019    -32150-1.98989E-0017-124.198108
NaBr  1.75775E-0017     705684-7.37056E-0019    -29591-1.83146E-0017-114.309551
KBr   1.59270E-0017     639422-6.67849E-0019    -26812-1.65949E-0017-103.576244
RbBr  1.52510E-0017     612282-6.39502E-0019    -25674-1.58905E-0017-99.180004
LiI   1.75107E-0017     703002-7.34255E-0019    -29478-1.82450E-0017-113.875175
NaI   1.62311E-0017     651632-6.80601E-0019    -27324-1.69117E-0017-105.554001
KI    1.48700E-0017     596987-6.23527E-0019    -25033-1.54936E-0017-96.702434
RbI   1.43100E-0017     574505-6.00045E-0019    -24090-1.49101E-0017-93.060617
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

9 additional negative charges in a cluster of 34 ions.
Perfect Cluster : af.cry
Defect Cluster  : af1.cry
ASCII-File      : af1.asc
   Perfect Cluster          Defect Cluster              Difference
  E/Cluster  E/mol        E/Cluster  E/mol       E/Cluster[J]  E/Cluster[eV]

LiF   2.98648E-0017    1057925-1.66011E-0018    -58807-3.15249E-0017-196.761434
NaF   2.59193E-0017     918161-1.44079E-0018    -51038-2.73601E-0017-170.766874
KF    2.24922E-0017     796758-1.25028E-0018    -44290-2.37424E-0017-148.187450
RbF   2.12799E-0017     753816-1.18289E-0018    -41903-2.24628E-0017-140.200703
LiCl  2.33998E-0017     828910-1.30073E-0018    -46077-2.47005E-0017-154.167308
NaCl  2.13229E-0017     755339-1.18529E-0018    -41987-2.25082E-0017-140.484078
KCl   1.91107E-0017     676974-1.06231E-0018    -37631-2.01730E-0017-125.909058
RbCl  1.82747E-0017     647358-1.01584E-0018    -35985-1.92905E-0017-120.400896
LiBr  2.18613E-0017     774411-1.21521E-0018    -43047-2.30765E-0017-144.031101
NaBr  2.01207E-0017     712753-1.11846E-0018    -39620-2.12392E-0017-132.563457
KBr   1.82314E-0017     645827-1.01344E-0018    -35900-1.92449E-0017-120.116165
RbBr  1.74576E-0017     618416-9.70423E-0019    -34376-1.84280E-0017-115.017897
LiI   2.00443E-0017     710044-1.11421E-0018    -39469-2.11585E-0017-132.059716
NaI   1.85796E-0017     658159-1.03279E-0018    -36585-1.96124E-0017-122.409748
KI    1.70215E-0017     602967-9.46182E-0019    -33517-1.79677E-0017-112.144688
RbI   1.63805E-0017     580259-9.10548E-0019    -32255-1.72910E-0017-107.921315
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

9 additional charges in a cluster of 36 ions.
Perfect Cluster : ag.cry
Defect Cluster  : ag1.cry
ASCII-File      : ag1.asc
   Perfect Cluster          Defect Cluster              Difference
  E/Cluster  E/mol        E/Cluster  E/mol      E/Cluster[J]  E/Cluster[eV]

LiF   3.12874E-0017      1046746 1.42765E-0019        4776-3.11446E-0017-194.387983
NaF   2.71540E-0017       908458 1.23904E-0019        4145-2.70300E-0017-168.706984
KF    2.35636E-0017       788338 1.07521E-0019        3597-2.34560E-0017-146.399926
RbF   2.22936E-0017       745850 1.01726E-0019        3403-2.21918E-0017-138.509520
LiCl  2.45144E-0017       820150 1.11859E-0019        3742-2.44026E-0017-152.307652
NaCl  2.23386E-0017       747357 1.01931E-0019        3410-2.22367E-0017-138.789477
KCl   2.00210E-0017       669820 9.13560E-0020        3056-1.99297E-0017-124.390270
RbCl  1.91452E-0017       640517 8.73595E-0020        2923-1.90578E-0017-118.948550
LiBr  2.29026E-0017       766227 1.04505E-0019        3496-2.27981E-0017-142.293713
NaBr  2.10792E-0017       705221 9.61843E-0020        3218-2.09830E-0017-130.964399
KBr   1.90999E-0017       639003 8.71529E-0020        2916-1.90127E-0017-118.667254
RbBr  1.82892E-0017       611881 8.34537E-0020        2792-1.82058E-0017-113.630484
LiI   2.09991E-0017       702541 9.58188E-0020        3206-2.09032E-0017-130.466734
NaI   1.94646E-0017       651204 8.88170E-0020        2971-1.93758E-0017-120.933169
KI    1.78323E-0017       596595 8.13690E-0020        2722-1.77510E-0017-110.791933
RbI   1.71608E-0017       574128 7.83046E-0020        2620-1.70825E-0017-106.619505
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

10 additional negative charges in a cluster of 40 ions.
Perfect Cluster : ah.cry
Defect Cluster  : ah1.cry
ASCII-File      : ah1.asc
   Perfect Cluster          Defect Cluster            Difference
  E/Cluster  E/mol        E/Cluster  E/mol     E/Cluster[J]  E/Cluster[eV]

LiF   3.60985E-0017    1086936-2.30375E-0018     -69366-3.84023E-0017-239.686296
NaF   3.13295E-0017     943338-1.99939E-0018     -60202-3.33289E-0017-208.020844
KF    2.71870E-0017     818607-1.73503E-0018     -52242-2.89220E-0017-180.515563
RbF   2.57217E-0017     774487-1.64152E-0018     -49426-2.73632E-0017-170.786452
LiCl  2.82841E-0017     851640-1.80504E-0018     -54350-3.00891E-0017-187.799968
NaCl  2.57737E-0017     776052-1.64483E-0018     -49526-2.74185E-0017-171.131647
KCl   2.30997E-0017     695538-1.47418E-0018     -44388-2.45739E-0017-153.376987
RbCl  2.20892E-0017     665110-1.40969E-0018     -42446-2.34989E-0017-146.667180
LiBr  2.64244E-0017     795647-1.68636E-0018     -50777-2.81108E-0017-175.452477
NaBr  2.43205E-0017     732298-1.55210E-0018     -46734-2.58726E-0017-161.483088
KBr   2.20369E-0017     663537-1.40636E-0018     -42346-2.34433E-0017-146.320334
RbBr  2.11016E-0017     635374-1.34667E-0018     -40548-2.24482E-0017-140.109844
LiI   2.42281E-0017     729515-1.54620E-0018     -46556-2.57743E-0017-160.869452
NaI   2.24577E-0017     676207-1.43321E-0018     -43154-2.38909E-0017-149.114277
KI    2.05744E-0017     619502-1.31303E-0018     -39536-2.18875E-0017-136.609824
RbI   1.97996E-0017     596171-1.26358E-0018     -38047-2.10632E-0017-131.465093
```

```
BORN 507 Conversion of a Crystallographic to Physical Files and
Calculation of Madelung Energies and Differences for all Alkali Halides

10 additional negative charges in a cluster of 42 ions.
Perfect Cluster : ai.cry
Defect Cluster  : ai1.cry
ASCII-File      : ai1.asc
   Perfect Cluster         Defect Cluster            Difference
  E/Cluster  E/mol       E/Cluster  E/mol    E/Cluster[J]  E/Cluster[eV]

LiF    3.70079E-0017    1061255 8.26360E-0019     23697-3.61816E-0017-225.825777
NaF    3.21187E-0017     921050 7.17187E-0019     20566-3.14015E-0017-195.991466
KF     2.78719E-0017     799266 6.22358E-0019     17847-2.72495E-0017-170.076754
RbF    2.63697E-0017     756188 5.88816E-0019     16885-2.57809E-0017-160.910256
LiCl   2.89966E-0017     831519 6.47473E-0019     18567-2.83491E-0017-176.939918
NaCl   2.64230E-0017     757717 5.90006E-0019     16919-2.58330E-0017-161.235489
KCl    2.36816E-0017     679105 5.28793E-0019     15164-2.31528E-0017-144.507540
RbCl   2.26456E-0017     649396 5.05660E-0019     14501-2.21400E-0017-138.185747
LiBr   2.70901E-0017     776848 6.04902E-0019     17346-2.64852E-0017-165.306455
NaBr   2.49332E-0017     714996 5.56741E-0019     15965-2.43765E-0017-152.144884
KBr    2.25921E-0017     647860 5.04464E-0019     14466-2.20876E-0017-137.858958
RbBr   2.16332E-0017     620362 4.83053E-0019     13852-2.11501E-0017-132.007607
LiI    2.48385E-0017     712279 5.54625E-0019     15905-2.42839E-0017-151.566734
NaI    2.30235E-0017     660231 5.14097E-0019     14742-2.25094E-0017-140.491334
KI     2.10928E-0017     604865 4.70986E-0019     13506-2.06218E-0017-128.709985
RbI    2.02984E-0017     582086 4.53248E-0019     12998-1.98452E-0017-123.862763
```

Appendix B

```
program BORN501;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 fRec: file of CrystPos;
 Pos : CrystPos;
 RecDat : String;
 IonN, n : Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                          BORN 501
');
  Writeln('
');
  Writeln('                 Generation of a new start cell
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                        Dr. Veit Marx
');
  Writeln('                          15.10.95
');
  Writeln('
');
  Writeln('                  Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
```

```
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 501 ');
  SchrT(14,5,5,'This program writes records with the
crystallographic ');
  SchrT(14,5,6,'coordinates a, b and c and the charge in a file.
');
  SchrT(14,5,8,'Please use the Extention .CRY        [RETURN]');
  Readln;
  ClrScr;
  SchrT(14,5,7,'Name of the File with Drive and Extention : ');
  SchrT(14,5,8,' eg A:FILENAME.CRY   : ');
  TextColor(11);
  Readln(RecDat);
  {$I-}
  SchrT(14,5,10,'Number of Ions : ');
  TextColor(11);
  repeat
   Readln(IonN);
  until IOResult=0;
  ClrScr;
  Assign(fRec,RecDat);
  Rewrite(fRec);
  For n:=1 to IonN do begin
   ClrScr;
   SchrT(14,5,2,'Ion number '); TextColor(11); Writeln(n);
   SchrT(14,5,4,'x       : '); TextColor(11);
   repeat
    Readln(Pos.a);
   until IOResult=0;
   SchrT(14,5,7,'y       : '); TextColor(11);
   repeat
    Readln(Pos.b);
   until IOResult=0;
   SchrT(14,5,10,'z       : '); TextColor(11);
   repeat
    Readln(Pos.c);
   until IOResult=0;
   SchrT(14,5,13,'charge  : '); TextColor(11);
   repeat
    Readln(Pos.charge);
   until IOResult=0;
   Write(fRec,Pos);
  end;
  {$I+}
  Close(fRec);
  TextColor(14); ClrScr;
 end.
```

```
program BORN502;

uses Crt;


type

CrystPos= record

A : Real;

B : Real;

C : Real;

Charge : Integer;
 end;


var

f1, f2: file of CrystPos;

Pos1, Pos2 : CrystPos;

RecDat1, RecDat2 : String;

FacN, nx, ny, nz : Integer;


procedure

SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string); begin
Textcolor(Fz); GotoXY(Ox, Oy); Write(Txt);

end;

begin

ClrScr;

TextBackground(LightGray); ClrScr;  Window(12,7,71,21);
TextBackground(Red);
TextColor(Yellow);
Writeln('
                                                ');

Writeln('
                              BORN 502
');
Writeln('
   ');
Writeln('                 Multiplication of the start cell
         ');
```

```
Writeln('
                    ');
Writeln('
                             ');
Writeln('
                                      ');
Writeln('
                                       Dr. Veit Marx
');
Writeln('
                                        15.10.95
');
Writeln('
                                                        ');
Writeln('                    Borland Turbo Pascal 6.0
  ');
Writeln('
          ');
Readln;
Window(1,1,80,25);
TextBackground(1);
ClrScr;
SchrT(14,30,2,'BORN 501 ');
SchrT(14,5,5,'This program builds a cluster by multiplication of
the start cell ');
SchrT(14,5,6,'by the factor n in three dimensions. ');
SchrT(14,5,8,'
         [RETURN]');
ClrScr;  SchrT(14,5,7,'Name of the Start-Cell-File with Drive and
Extention : ');
SchrT(14,5,8,'
eg A:NAME1.CRY    : ');
TextColor(11);
Readln(RecDat1);
SchrT(14,5,10,'Name of the Cluster-File with Drive and Extention
: ');
SchrT(14,5,11,' eg A:NAME2.CRY    : ');
TextColor(11);
Readln(RecDat2);

$I-}
SchrT(14,5,13,'Factor n : ');
TextColor(11);
repeat
Readln(FacN);  until IOResult=0;
ClrScr;
Assign(f1,ReCDat1);
Assign(f2,RecDat2);
Rewrite(f2);
For nx:=1 to FacN do begin
For ny:=1 to FacN do begin
For nz:=1 to FacN do begin
Reset(f1);
While not EOF(f1) do begin
Read(f1,Pos1);
Pos2.A:=Pos1.A + nx-1;       Pos2.B:=Pos1.B + ny-1;
Pos2.C:=Pos1.C + nz-1;       Pos2.Charge:=Pos1.Charge;
Write(f2,Pos2);
end;
```

```
Close(f1);
   end;
  end;
 end;
{$I+}
Close(f2);
TextColor(14);
ClrScr;
end.
```

→

```
program BORN503;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1, f2: file of CrystPos;
 Pos1, Pos2 : CrystPos;
 RecDat1, RecDat2 : String;
 LC: Real;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                       BORN 503
');
  Writeln('
');
  Writeln('           Conversion of a crystallographic
');
  Writeln('                  to a physical file
');
  Writeln('
');
  Writeln('
');
  Writeln('                     Dr. Veit Marx
');
  Writeln('                       17.10.95
');
  Writeln('
');
  Writeln('               Borland Turbo Pascal 6.0
');
  Writeln('
');
  Readln;
```

```
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 503 ');
  SchrT(14,5,5,'This program converts a file with ion positions in
crystallographic ');
  SchrT(14,5,6,'coordinate system into a file with ion positions
in physical coordinate ');
  SchrT(14,5,7,'system with the unit Angstrom.');
  SchrT(14,5,8,'Only for cubic system!');
  SchrT(14,5,9,'
[RETURN]');
  ClrScr;
  SchrT(14,5,7,'Name of the Crystallographic File with Drive and
Extention : ');
  SchrT(14,5,8,' eg A:NAME1.CRY    : ');
  TextColor(11);
  Readln(RecDat1);
  SchrT(14,5,10,'Name of the Physical File with Drive and
Extention : ');
  SchrT(14,5,11,' eg A:NAME2.PHY    : ');
  TextColor(11);
  Readln(RecDat2);

  {$I-}
  SchrT(14,5,13,'Lattice constant in Angstrom : ');
  TextColor(11);
  repeat
   Readln(LC);
  until IOResult=0;
  ClrScr;
  Assign(f1,ReCDat1);
  Assign(f2,RecDat2);
  Reset(f1);
  Rewrite(f2);
  While not EOF(f1) do begin
   Read(f1,Pos1);
   Pos2.A:=Pos1.A*LC;
   Pos2.B:=Pos1.B*LC;
   Pos2.C:=Pos1.C*LC;
   Pos2.Charge:=Pos1.Charge;
   Write(f2,Pos2);
  end;
  {$I+}
  Close(f1);
  Close(f2);
  TextColor(14); ClrScr;
 end.
```

```
program BORN504;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1, f2: file of CrystPos;
 Pos1, Pos2 : CrystPos;
 RecDat1, RecDat2 : String;
 NewX, NewY, NewZ: Real;
 NewCharge, n, DelN, ChaN, MenuN : Integer;
procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                        BORN 504
');
  Writeln('
');
  Writeln('            Modification of a physical file
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                      Dr. Veit Marx
');
  Writeln('                        18.10.95
');
  Writeln('
');
  Writeln('                Borland Turbo Pascal 6.0
');
  Writeln('
');
```

```
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 504 ');
  SchrT(14,5,5,'This program changes single ion positions to put
defects ');
  SchrT(14,5,6,'or additional charges in the cluster.');
  SchrT(14,5,9,'
[RETURN]');
  ClrScr;
  SchrT(14,5,7,'Name of the Start File with Drive and Extention :
');
  SchrT(14,5,8,' eg A:NAME1.PHY   : ');
  TextColor(11);
  Readln(RecDat1);
  SchrT(14,5,10,'Name of the modified File with Drive and
Extention : ');
  SchrT(14,5,11,' eg A:NAME2.PHY   : ');
  TextColor(11);
  Readln(RecDat2);
  ClrScr;
  SchrT(14,30,2,'MODIFICATION');
  SchrT(14,5,5,'1  Insert of an additional ion position');
  SchrT(14,5,7,'2  Delete of an ion position');
  SchrT(14,5,9,'3  Change of an ion position                 : ');
  {$I-}
  TextColor(11);
  repeat
   Readln(MenuN);
  until IOResult=0;
  ClrScr;
  Assign(f1,RecDat1);
  Assign(f2,RecDat2);
  If MenuN=1 then begin
   Reset(f1);
   Rewrite(f2);
   While not EOF(f1) do begin
    Read(f1,Pos1);
    Write(f2,Pos1);
   end;
   TextBackground(2); ClrScr;
   SchrT(15,30,2,'NEW ION POSITION');
   SchrT(15,5,5,'X : ');
   repeat
    Readln(Pos2.A);
   until IOResult=0;
   SchrT(15,5,7,'Y : ');
   repeat
    Readln(Pos2.B);
   until IOResult=0;
   SchrT(15,5,9,'Z : ');
   repeat
    Readln(Pos2.C);
   until IOResult=0;
   SchrT(15,5,11,'Charge : ');
   repeat
    Readln(Pos2.Charge);
   until IOResult=0;
   Write(f2,Pos2);
```

```
program BORN505;
{$N+}
uses
 Crt;
type
 CrystPos = record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 f1: file of CrystPos;
 Pos : CrystPos;
 RecDat, AsciiDat: String;
 fText : Text;
 n, m, p : Integer;
 ArA, ArB, ArC: Array[1..2000] of Real;
 ArCharge :Array[1..2000] of Integer;
 AtomN: Integer;
 ka1, kb1, kc1, ka2, kb2, kc2, charge1, charge2: Real;
 r, Abst, Summe, Ec, Er, Ergebnis, Cluster: real;
 yn: char;
 k: Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                        BORN 505
');
  Writeln('
');
  Writeln('           Calculation of the Madelung energy
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                        Veit Marx
');
```

```
  Writeln('                          26.10.1995
');
  Writeln('
');
  Writeln('
');
  Writeln('                   Borland  TURBO PASCAL 6.0
');
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 505 ');
  SchrT(14,5,5,'This program calculates the Madelung energy of a
cluster ');
  SchrT(14,5,6,'in a physical file.');
  SchrT(14,5,7,'Input data and results are written in an ASCII-
File.');
  SchrT(14,5,8,'
RETURN  ');
  Readln;
  ClrScr;
  SchrT(14,30,2,'INPUT DATA');
  SchrT(14,5,4,'Name of the physical file with drive and extention
: ');
  SchrT(14,5,5,'  eg A:NAME1.PHY : '); TextColor(11);
  Readln(RecDat);
  SchrT(14,5,7,'New ASCII-File ?  y/n  : '); TextColor(11);
  Readln(YN);
  SchrT(14,5,9,'Name of the ASCII file with drive and extention :
');
  SchrT(14,5,10,'  eg A:NAME2.ASC : '); TextColor(11);
  Readln(AsciiDat);
  ClrScr;
  Assign(fText,AsciiDat);
  If yn='y' then Rewrite(fText);
  If yn='n' then Append(fText);
  Writeln(fText,'BORN 505 Madelung energy calculation ');
  Writeln(fText,RecDat);
  Assign(f1,RecDat);
  Reset(f1);
  m:=0;     k:=0;
  While not EOF(f1) do begin
   Read(f1,Pos);
   m:=m+1;
   ArA[m]:=Pos.A;
   ArB[m]:=Pos.B;
   ArC[m]:=Pos.C;
   ArCharge[m]:=Pos.Charge;
   AtomN:=m;
  end;
  Close(f1);
  Summe:=0;
  For m:=1 to AtomN do begin
   ka1:=ArA[m];
   kb1:=ArB[m];
   kc1:=ArC[m];
   charge1:=ArCharge[m];
   For p:=1 to AtomN do begin
    ka2:=ArA[p];
```

```
    kb2:=ArB[p];
    kc2:=ArC[p];
    charge2:=ArCharge[p];
    Abst:=(ka2-ka1)*(ka2-ka1)+(kb2-kb1)*(kb2-kb1)+(kc2-kc1)*(kc2-
kc1);
    If Abst>0.01 then begin
     Abst:=SQRT(Abst);
     r:=Abst*1E-10;
     Ec:= (charge1*charge2*2.3070794E-28)/r;
     Summe:=Summe+Ec;
     k:=k+1;
     Cluster:=Summe/2;
    end;
   end;
  end;
  Ergebnis:=-(Summe*6.02205E23)/(AtomN);
  Write('Coulomb-Energy in J/mol NaCl '); Writeln(Ergebnis);
  Write('Coulomb-Energy in J/Cluster  '); Writeln(Cluster);
  Write(fText,'Coulomb-Energy in J/mol : ');
Writeln(fText,Ergebnis);
  Write(fText,'Coulomb-Energy in J/Cluster: ');
Writeln(fText,Cluster);
  Writeln(fText,' ');
  Readln;
  Close(fText);
end.
```

```
program BORN506;
uses
 Crt;

type
 CrystPos= record
  A : Real;
  B : Real;
  C : Real;
  Charge : Integer;
 end;

var
 fRec: file of CrystPos;
 Pos : CrystPos;
 RecDat : String;
 IonN, n : Integer;

procedure SchrT(Fz: Byte; Ox: Byte; Oy: Byte; Txt: string);
 begin
 Textcolor(Fz);
 GotoXY(Ox, Oy);
 Write(Txt);
 end;

begin
  ClrScr;
  TextBackground(LightGray); ClrScr;
  Window(12,7,71,21);
  TextBackground(Red);
  TextColor(Yellow);
  Writeln('
');
  Writeln('                       BORN 506
');
  Writeln('
');
  Writeln('                       Show File
');
  Writeln('
');
  Writeln('
');
  Writeln('
');
  Writeln('                     Dr. Veit Marx
');
  Writeln('                       15.10.95
');
  Writeln('
');
  Writeln('               Borland Turbo Pascal 6.0
');
  Writeln('
');
```

```
  Readln;
  Window(1,1,80,25);
  TextBackground(1); ClrScr;
  SchrT(14,30,2,'BORN 506 ');
  SchrT(14,5,5,'This program shows the records of a
crystallographic or of a');
  SchrT(14,5,6,'physical file on monitor. ');
  SchrT(14,5,8,'
[RETURN]');
  Readln;
  ClrScr;
  SchrT(14,5,7,'Name of the File with Drive and Extention : ');
  SchrT(14,5,8,' eg A:FILENAME.CRY   : ');
  Readln(RecDat);
  ClrScr;
  SchrT(14,1,1,'No    a or x          b or y         c or z
charge    [RETURN]');
  Writeln;
  TextColor(11);
  Assign(fRec,RecDat);
  Reset(fRec);
  n:=0;
  While not EOF(fRec) do begin
   n:=n+1;
   Read(fRec,Pos);
   Write(n);
   Write('     ');
   Write(Pos.A:8:6);
   Write('        ');
   Write(Pos.B:8:6);
   Write('       ');
   Write(Pos.C:8:6);
   Write('    ');
   Write(Pos.Charge);
   Readln;
  end;
  Close(fRec);
  TextColor(14); ClrScr;
 end.
```

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