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Domain Model for Anomalously Fast Diffusion

W. VAN GOOL AND P. H. BOTTELBERGHS

Department of Inorganic Chemistry, State University of Utrecht, Netherlands

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Electrostatic calculations are performed in idealized β-Al_2O_3, containing domains with displaced sodium ions. The average additional energy per sodium ion is calculated for several sizes and shapes of the domains. The movement of the domain walls is considered to be essential in the process of anomalously fast conduction. The electrostatic energy contribution to the activation energy for wall movement is calculated. Some rules are formulated which might permit the selection of possible super ionic conductors by electrostatic calculations in ionic compounds.

1. Introduction

In a previous paper (*1*) it was emphasized that anomalously fast diffusion in crystalline solids requires an explanation different from the usual diffusion mechanisms in slightly defective materials. Cooperative aspects are of predominant importance. It was also suggested that the observation of having more equivalent sites in the crystal structure than corresponds to the number of migrating ions in good ionic conductors is as such not an explanation. Although rather complicated models are presently under investigation, a less rigorous approach might be helpful in the process of materials selection.

One suggestion to describe the anomalously fast diffusion mode was by means of domains. In this paper we want to explore some aspects of the domain model. In the next section the use of the domain model is discussed in connection with anomalously fast diffusion. Calculations of the electrostatic energy of domains in an idealized β-Al_2O_3 structure are reported. Finally the limitation of the significance of these calculations is stressed and their use in connection with other materials is outlined.

2. Domain Model

The basic ideas of the domain model are best illustrated with an example, such as idealized β-Al_2O_3. The ideal structure of β-Al_2O_3 which corresponds to the composition $Na_2O_3 \cdot 11Al_2O_3$ has been described several times (*2–7*). Blocks of spinal types alumina are separated by Na–O layers. The oxygen functions as spacers between the blocks and sodium migration occurs in this layer (*8*). The sodium ions can be in two different positions, the so-called Beevers Ross (BR) sites and anti Beevers Ross (aBR) sites (*3*). With all Na-ions in one of the two positions, two different structures are obtained which are not equivalent. The differences are however small as can be seen from the electrostatic energy of the two structures. This leads to the description of two available sites for each sodium ion, which is the structural condition referred to the introduction.

With all Na^+-ions in the BR position $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ (Fig. 1), lattice self-potentials (potentials at lattice sites) and lattice potentials (potentials at interstitial sites) were calculated with the Ewald procedure (*10*) in a computerized form (*9*). From these calculations $V_{BR} = -0.885$ e/Å and $V_{aBR} = -0.740$ e/Å is obtained (for both calculations the sodium ion at the BR-site was removed). Thus it requires 2.08 eV (or 49.0 kcal/mol) to bring one Na^+ to an aBR site in the BR configuration. This demonstrates that having two sites available for each Na^+ ion does not guarantee that displacement of only one ion is energetically inexpensive.

Note that all energies quoted are electrostatic energies involving fixed ion positions. In order to arrive at the values of internal energy, a number of corrections must be applied; for example Born repulsion, van der Waals–London energy, zero point energy (*11*). Generally these corrections

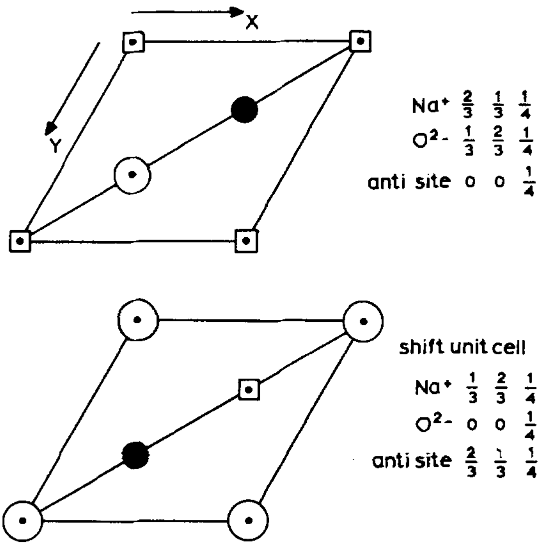


FIG. 1. Two different descriptions of the unit-cell in the Na–O layer in β-Al_2O_3.

do not exceed 20–25% of the original electrostatic energy. In energy differences between comparable situations they largely cancel. More important might be the relaxation of the fixed positions and the influence thereof on the lattice vibrations. Such refinements are outside the scope of this approach.

The only way to decrease the energy between initial and final state of the diffusion step, is to consider larger domains of displaced ions. The domain concept has been used extensively for the description of disordered crystals (*12–21*). Regularly shaped domains can be detected by several techniques, but the occurrence of irregularly shaped domains is more difficult to establish (*17*). However, they have been used in several papers (*15*, *20*).

The displacement of domains of Na-ions to interstitial sites decreases the energy necessary to create the defect situation. Obviously, when all Na-ions are displaced to the anti-sites, we have again the original situation (not exactly so in β-Al_2O_3). Thus the essential question is what size the domain must have in order to get a small energy difference when diffusion occurs, the latter entailing a change of the domain site and shape. Using regular domains in the form of mosaic blocks, energy calculations were performed in the block (Fig. 2). Suppose n_t is the number of displaced ions in the block, q_{Na} the charge of the sodium ions, N and K indicators for

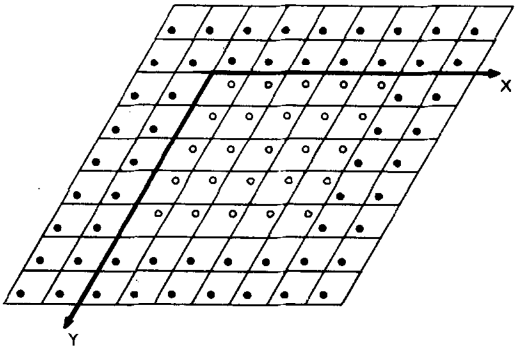


FIG. 2. Mosaic block of Na^+-ions at anti-sites

the original positions of the Na-ions, V_{Na} and $V_{\mathrm{Na},i}$ potentials at the Na-positions (self-potential) and at the new positions in the original lattice, then V_{ki}, the potential at position k in the block is given by

$$V_{k,i} = V_{\mathrm{Na},i} + q_{\mathrm{Na}}\left[\sum_{N}{}' 1/r_{NK} - \sum_{N} 1/r_{Nk}\right] \qquad (1)$$

and the average energy difference per ion $E_2 - E_1$ between block and original structure by

$$E_2 - E_1 = q_{\mathrm{Na}}[V_{\mathrm{Na}} - V_{\mathrm{Na},i}] +$$
$$+ (q_{\mathrm{Na}}^2/n_t)\left[\sum_{N}\sum_{k} 1/r_{N,k} - \sum_{N}\sum_{K}{}' 1/r_{NK}\right] \qquad (2)$$

$\sum_N \sum_K{}'$ indicates that the situation $N = K$ is excluded from the summation; distances r_{NK} and r_{Nk} are indicated in Fig. 3. For a proof of Eqs. (1) and (2) see Appendix 1.

The calculated values $E_2 - E_1$ for a number of differently sized mosaic blocks are summarized in Table I. This table shows how fast the average energy decreases with the size of the block, with a slight dependence on the shape of the blocks.

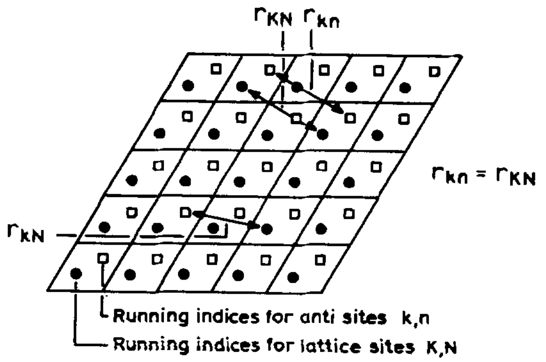


FIG 3. Distances in the mosaic block used in the calculations.

TABLE I

AVERAGE ELECTROSTATIC ENERGY OF DOMAINS IN eV MOLECULE^{-1}

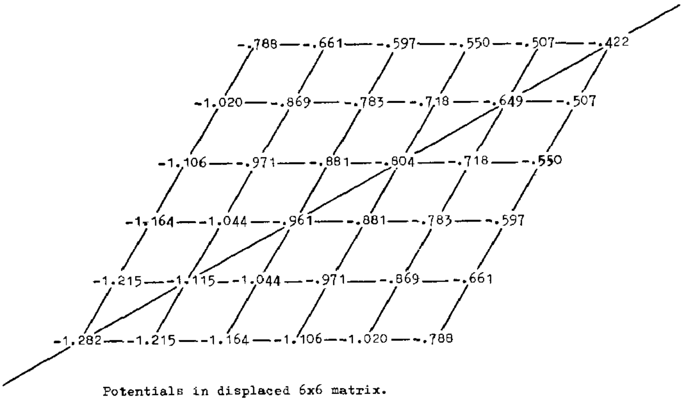
Matrix	n_t	Av. en.	High[a]	Low[a]
1 × 1	1	−2.084	−0.740	−0.740
1 × 2	2	−1.589	−0.871	−0.679
1 × 3	3	−1.376	−0.898	−0.660
1 × 4	4	−1.261	−0.910	−0.652
2 × 2	4	−1.169	−1.054	−0.591
1 × 5	5	−1.189	−0.916	−0.646
1 × 6	6	−1.139	−0.920	−0.643
2 × 3	6	−0.978	−1.100	−0.561
1 × 7	7	−1.103	−0.923	−0.641
1 × 8	8	−1.075	−0.925	−0.639
2 × 4	8	−0.867	−1.120	−0.545
3 × 3	9	−0.798	−1.156	−0.523
2 × 5	10	−0.795	−1.131	−0.536
2 × 6	12	−0.744	−1.139	−0.530
3 × 4	12	−0.692	−1.182	−0.503
2 × 7	14	−0.706	−1.144	−0.526
3 × 5	15	−0.621	−1.198	−0.490
4 × 4	16	−0.588	−1.213	−0.479
2 × 8	16	−0.677	−1.147	−0.522
3 × 6	18	−0.570	−1.208	−0.482
4 × 5	20	−0.519	−1.232	−0.464
3 × 7	21	−0.532	−1.215	−0.476
3 × 8	24	−0.502	−1.220	−0.471
4 × 6	24	−0.469	−1.244	−0.454
5 × 5	25	−0.450	−1.252	−0.447
4 × 7	28	−0.431	−1.253	−0.446
4 × 8	32	−0.401	−1.260	−0.440
6 × 6	36	−0.352	−1.283	−0.422
7 × 7	49	−0.278	−1.307	−0.401
8 × 8	64	−0.220	−1.327	−0.383
9 × 9	81	−0.172	−1.343	−0.368

[a] High and low are the extreme values of potentials at aBR-sites in the domain. (Potentials in e/Å.)

For diffusion it is important to calculate the differential energy, that is the average energy per additional ion when the size of the block is increased. From Table I it is easily calculated that an increase from, for example, a 3 × 4 block to a 4 × 4 block, the differential average energy for the last 4 ions involves 0.252 eV molecule^{-1}. This is 1/8 of the energy necessary to displace one single ion in a regular structure.

Although these calculations can be extended in several ways, the importance of the results is limited for several reasons (see next section). However, three aspects should be stressed here. First the importance of the foregoing calculations is that relatively small blocks are already sufficient to bring the energy for displacement down to values necessary for anomalously fast migration. Second, the potential distribution in the block shows interesting features. This is demonstrated in Fig. 4, where such a distribution is plotted for a 6 × 6 block. This potential distribution can be understood from the excess positive charge along two boundaries of the block, and the lack of positive charge along the other two boundaries (Fig. 2). Energetically more favourable but less regular forms might be devised (Fig. 5).

In order to explain the transport of Na-ions through the material movement of the domain walls must be assumed. In other descriptions the movement of domain walls has been assumed in order to explain changes in structures. For diffusion a fast movement of the walls is necessary. According to general kinetic principles the energy loss (polarization) during the transport will be low only when the net flow is low compared to the equilibrium exchange. Interpreted for the domain situations this means that the



Potentials in displaced 6x6 matrix.

FIG. 4. Potentials at anti-sites in a 6 × 6 regular mosaic block.

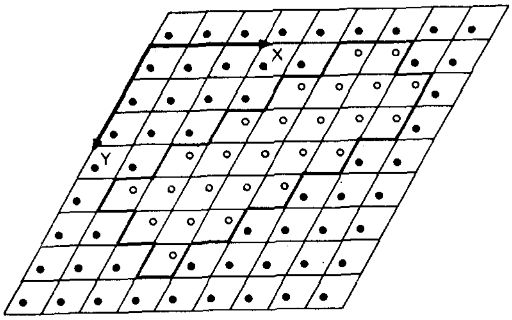


FIG. 5. Irregularly shaped domain: excess charges along walls of domain are less pronounced than in the situation represented in Fig. 2.

domain walls are moving in all directions maintaining an equilibrium distribution of domain sizes, whereas an electrical potential gradient or a chemical potential gradient gives a slight excess of Na-transport in one direction.

Figure 6 shows one domain wall. Movement of this wall gives a Na-transport. In order to maintain a current of 100 mA/cm^2 with a potential gradient of 1 V/cm, the velocity of the wall must be of the order of 10^4 cm/sec. Assuming that this current density does not yet produce polarization effects in the bulk material, the equilibrium velocity must be at least 10^5–10^6 cm/sec. The movement of the wall is a spatially cooperative phenomena, but not necessarily timely cooperative. With spatially cooperative is meant that once a section of the wall has moved, the remainder of the wall will move without increasing the Gibbs free energy. This is a method to fulfill the thermodynamic condition for fast ion transport.

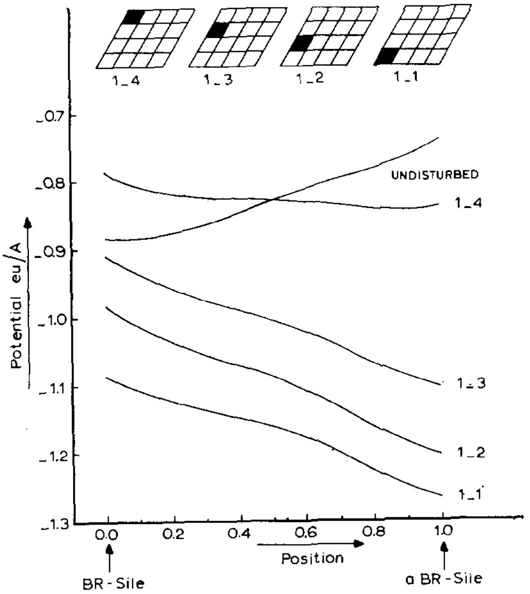


FIG. 7. Potential distribution along the line connecting BR-site and anti BR-site in different unit cells. Position is indicated as a fraction of the BR–aBR distance. Numbering of unit cells indicated at the top of the figure. Outside the mosaic block all Na$^+$-ions occupy BR-sites. Undisturbed curve: all Na$^+$-ions are in BR-sites (no mosaic block present).

The fulfillment of the kinetic condition for fast fluctuations of domain shapes can be checked by electrostatic calculations. The structure of β-Al_2O_3 is such that already the displacement of one Na$^+$-ion in a complete ordered structure involves a passage through a potential distribution without a maximum (*9*, Fig. 1, p. 108). Compare the corresponding calculations for

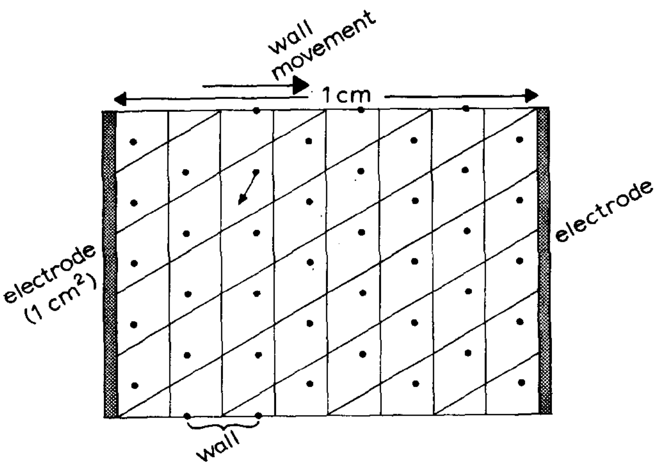


FIG. 6. Wall movement in idealized β-Al_2O_3.

cooperative movement of protons of KHF_2 where a distinct maximum occurs (*22*). What must be checked is the question if the domain has not influenced this potential gradient unfavourably.

Suppose, for example, that 3×4 mosaic growths to a 4×4 mosaic by displacing a wall. Assume that 3 of the 4 Na^+-ions have been displaced already and that the last ion is in one of the unit-cells 1-1 to 1-4 (see Fig. 7). The electrostatic potential distribution in each of these situations was calculated, moving from the BR-site to the corresponding aBR-site. Figure 7 shows indeed that the mosaic block already present does influence the potentials, but no activation energy due to the electrostatic field is created. This means that either of the four ions tends to complete the 4×4 block without being hampered by an electrostatic energy mountain. On the other hand, a 4×4 block could start most favourably in the corner 1-4 when the size must be decreased.

3. Discussion

Summarizing the proposed model for anomalously fast conduction one has the following features.

(1) One of the major constituents of the material has available more than the necessary number of sites in the crystal structure. This constituent will become the migrating species.

(2) Occupying the available sites in a regular way, one has to calculate whether the displacement of one ion to a so-called equivalent site leads to a substantially higher energy state. If not, the structural situation is favourable for fast migration.

(3) When displacement of one ion leads to a higher energy state, the cooperative displacement of a number of ions must be checked. Due to the definition of equivalent sites in time-averaged structures, the average energy for a number of displaced ions will always approach zero when this number becomes large. These calculations aim at finding the smallest size of the displaced domains having low enough average energy per ion to arrive at fast diffusion.

(4) For the situations mentioned under 2 and 3 the activation energy for the displacement of one ion or a domain wall must be calculated. When this activation energy is low the situation has a high equilibrium exchange, e.g. fast moving walls in the domain model. Then anomalously fast conduction can be expected.

The electrostatic energy calculations are only the first step towards the evaluation of thermodynamic quantities. A complete statistical mechanical evaluation has to be performed for a full description. There are, however, several reasons why this evaluation is not of very much practical value for idealized β-Al_2O_3. First it is not the material used as ionic conductor in batteries. The applied material has an important excess of Na^+. The limit for excess Na^+ is found in another idealized structure, viz. β''-Al_2O_3 ($Na_2O \cdot MgO \cdot 5Al_2O_3$). Here both normal and anti sites are occupied (*23*). The materials somewhere between β- β''-Al_2O_3 are of interest. Recent X-ray interpretations do not lead to a simple occupation of BR and aBR-sites (*5*, *6*). However, another problem occurs with respect to the charge compensation of the additional Na^+. The defect chemistry is not yet fully understood. Thus additional assumptions have to be made about the defect situation. Furthermore, the domain concept requires a certain amount of remodelling when an excess of Na^+ is present. Calculations are presently performed for the situation half-way between β- and β''-Al_2O_3. Here 50% excess of Na^+ compared to β-Al_2O_3 is present.

A more detailed analysis of the "half-way" composition might finally lead to the interpretation of the relevant properties, e.g. the correlation factor in the diffusion process. We point out, however, that the aim of the developed model is selection of new anomalously good conductors, and not the detailed description of one special material.

It is gratifying to see that a detailed structure analysis by Roth (*6*) leads to descriptions very comparable to those given in this paper. This is interesting since the starting points are different, viz. the time averaged structure data and electrostatic calculations in specified configurations. A remaining problem is the relationship between the fast fluctuating domains and the observed X-ray data.

In recent years several approaches have been used to describe the cooperative aspects of fast diffusion. For example, Sato and Kikuchi (*24*, *25*) give a detailed statistical mechanical analysis of the disordered sodium configurations. The treatment is based upon a very simple relationship between sodium configuration and energy. In view of the predominance of the long range electrostatic forces, this basic assumption might need further amplification.

In another recent approach, Rice and Roth

(*26*) assume the sodium ions to move freely, once an energy gap has been overcome. This model is not in contradiction to the approach followed in the present paper. Fast moving walls of small mosaic blocks mean that for a number of phenomena the sodium ions behave as a liquid or a gas.

It should be stressed, however, that the present description is developed for materials selection mainly. The conditions 1-4 mentioned in the beginning of this discussion can be checked when the materials are predominantly ionic.

Appendix

Derivation of Formulas (1) and (2)

Equation (1) is rather obvious. The potential at site k is equal to the potential at the anti-site k due to the undisturbed lattice ($V_{\mathrm{Na},i}$) plus the corrections due to the displacement in the mosaic block (Fig. 3). There are two corrections. One originates from the Na^+-ions in their new positions. This leads to

$$q_{\mathrm{Na}} \sum_n{}' (1/r_{nk}) = q_{\mathrm{Na}} \sum_N{}' (1/r_{NK}).$$

With k and n position indices for the anti-sites, and K and N corresponding indices for lattice sites, the relation $r_{nk} = r_{NK}$ is obvious. The prime indicates $n \neq k$ or $N \neq K$.

The other correction stems from the removed potential contribution of the Na^+ on their original sites: $-q_{\mathrm{Na}} \sum_N{}' (1/r_{Nk})$. Now point K is included in the summation, since we use $V_{\mathrm{Na},i}$ as the potential on an interstitial site with the neighbouring Na^+ present.

Equation (2) is less obvious. Dividing the lattice in sections IN (all points in the mosaic block, from which the Na^+-ions are displaced) and OUT (all points in their original position outside the mosaic block), then it must be shown that the interaction energy between IN and OUT is properly included in Eq. (2). This can be demonstrated in the following way.

Assume a mosaic block in only one Na^+-layer in β-$\mathrm{Al_2O_3}$, All interactions are of the type $-\frac{1}{2} \sum_i \sum_j{}' (q_i q_j)/r_{ij}$. Here the factor $\frac{1}{2}$ has to be used only when the double summation refers to one set of ions (viz. the Na^+-ions in the block) since all interactions have been counted twice. In that case the prime indicates $j \neq i$. When the two sets are different, both the factor $\frac{1}{2}$ and the prime are left out, thus $- \sum_i \sum_j (q_i q_j)/r_{ij}$.

To shorten the notation, charges and distances are left out. They can always be inferred from the symbols underneath the summation sign.

Then the electrostatic energy for the undisturbed lattice is

$$E_1 = -\tfrac{1}{2} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}}{}' - \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} - \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Al}} - \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{O}} + \text{(other terms)} \qquad \text{(A-1)}$$

Other terms refer to all summations, like $\sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} \sum\limits_{\mathrm{Al}}$ etc., which will not change when the mosaic is formed. $\sum\limits_{\mathrm{Al}}$ includes all aluminium ions, irrespective of their location.

After the formation of the mosaic we have mosaic we have

$$E_2 = -\tfrac{1}{2} \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}}{}' - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Al}} - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{O}} + \text{(other terms)} \qquad \text{(A-2)}$$

Although the first term in each equation refer to different summations, the numerical result is the same, since $r_{nk} = r_{NK}$ (see Fig. 3). Therefore these terms, together with "other terms" cancel in the formation of $E_2 - E_1$

$$E_2 - E_1 = - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Al}} - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{O}} + \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} + \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Al}} + \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{O}} \qquad \text{(A-3)}$$

The following manipulation is performed in order to arrive at interactions between IN and OUT expressed as potentials. We add to (A-3)

$$- \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}}{}' + \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}}{}' - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} + \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \; (= 0) \text{ and we use}$$

$$\sum\limits_{\mathrm{Na}}^{\mathrm{IN}} + \sum\limits_{\mathrm{Na}}^{\mathrm{OUT}} = \sum\limits_{\mathrm{Na}}$$

$$E_2 - E_1 = - \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} \Bigl(\sum\limits_{\mathrm{Na}} + \sum\limits_{\mathrm{Al}} + \sum\limits_{\mathrm{O}} \Bigr) + \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \Bigl(\sum\limits_{\mathrm{Na}}{}' + \sum\limits_{\mathrm{Al}} + \sum\limits_{\mathrm{O}} \Bigr) + \Bigl(\sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}_i}^{\mathrm{IN}} - \sum\limits_{\mathrm{Na}}^{\mathrm{IN}} \sum\limits_{\mathrm{Na}}^{\mathrm{IN}}{}' \Bigr) \qquad \text{(A-4)}$$

Now $\sum\limits_{\text{Na}} + \sum\limits_{\text{Al}} + \sum\limits_{\text{O}}$ for the Na_i-site is the interstitial potential $V_{\text{Na},i}$ at that site, in the regular lattice (no mosaic blocks). Thus it has the same value for all the interstitial sites in the mosaic block. Correspondingly, the second term in (A-4) gives the self-potential at the Na^+-site. Using n_t for the number of displaced ions and introducing charges and distances left out so far:

$$E_2 - E_1 = -n_t q_{\text{Na}} V_{\text{Na},i} + n_t q_{\text{Na}} V_{\text{Na}} + + q_{\text{Na}}^2 \left\{ \sum_N \sum_K (1/r_{Nk}) - \sum_N \sum_K{}' (1/r_{NK}) \right\} \tag{A-5}$$

which is Eq. (2).

It is true that energies in the summation $\sum\limits_N \sum\limits_K{}' (1/r_{\text{NK}})$ are counted twice, but the same double counting has been used with opposite sign in the potential expression by multiplying the potential at Na^+-sites with the number of sites. V_{Na} and $V_{\text{Na},i}$ are obtained as output of the general computer program for undisturbed lattices. For Eq. (A-5) an additional program was used.

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