Molecular dynamics simulation as a complement to diffraction in the study of disorder in crystals

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SUMMARY

It is not uncommon that a crystal structure contains a minority component which does not share the overall space-group of the remainder of the structure, but has a lower (or no) effective space-group symmetry. A conventional diffraction treatment will inevitably be made within the space-group of the majority of the system, and will therefore result in an average structure also with this symmetry. We here indicate the value of molecular dynamics (MD) simulation within a supercell of the structure as a complementary tool in providing information concerning the local structure for the minority component. Such information, though illusive, is often the most interesting and the physically most significant aspect of the structure. It can also be crucial information for the testing of new theory, and in the design of new materials. The approach is illustrated for the case of the Na^+ ion distribution in Na^+ β''-alumina, and for the experimentally more inaccessible mixed-ion system Na^+/Ba^{2+} β''-alumina.

INTRODUCTION

It often happens that a crystallographic study of a material results in a structure whose major part can be described satisfactorily within some given space-group, but which also contains some minority component with a lower symmetry, or with no obvious symmetry at all. Situations of this kind can be expected in structural studies of physically interesting disordered materials such as zeolites, metal hydrides, or solid electrolytes (e.g. Refs. 1–3).

The normal crystallographic approach in such situations is to carry out the diffraction datacollection, processing, structure determination and subsequent refinement within the space-group of the majority of the structure. Space-group forbidden, intermediate superlattice and/or extra diffuse reflections are often too weak to be observed (typically, if the atoms which break the sym-

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metry are hydrogens in an X-ray study), or are conveniently neglected in a conventional diffraction experiment. The ultimate result is a valid observation of the 'well behaved' majority structure, onto which is superposed a space-group-constrained, time-averaged representation of the lower symmetry minority component.

A more ambitious diffraction treatment, aimed at providing a more detailed structural picture, can involve refinement in some lower space-group, or employ some appropriate superlattice [4]. Disorder diffuse scattering (DDS) studies [5], or the use of high-resolution electron microscopy techniques [6] can also provide extra information. Certainly, if no extra diffraction information is available in the form of 'forbidden reflections', etc., then it can be argued that an average of the type described gives a valid picture of a truly randomly disordered system and that, indeed, we can go no further experimentally. On the other hand, some functionally significant local ordering phenomenon can still be present with a characteristic correlation length shorter than the intrinsic diffraction coherence length, and thus appear 'random' in the diffraction experiment (see Ref. 7). In such a situation, the structural chemist is at a loss to attain more meaningful experimental information. A theoretical molecular dynamics approach of the type outlined here can prove a powerful complement and, moreover, contribute strongly to the predictive usefulness of the structural information derived.

THE PRINCIPLE OF MOLECULAR DYNAMICS

The advent of supercomputers has facilitated the development of a number of new and powerful theoretical techniques. One of the more important of these is molecular dynamics (MD). Although MD techniques are still under development, they are already being applied in many diverse areas of materials science. The present approach to the study of ordering phenomena in crystalline materials is such an area. For a general review of the MD method as applied to condensed matter, see Ref. 8.

The basic principle of molecular dynamics is essentially trivial: a number of interacting particles are arranged in a 'simulation box' which, for our purposes, will be typically an integer number of juxtaposed crystallographic unit-cells; as many as are considered necessary and practicable. This 'box' is then repeated periodically in three dimensions to create an infinite array. Modifications to this general procedure can clearly be made to simulate a crystal surface [9], or a finite crystallite [10]. The particles enclosed within the simulation box are allowed to interact with one another and with all their images, normally according to pairwise interaction potentials. In the illustrative example given later, interactions were assumed to have the following Buckingham form:

$$V_{\alpha\beta}(r) = Q_\alpha Q_\beta / r + A_{\alpha\beta} \exp\left(-r/\gamma_{\alpha\beta}\right) - C_{\alpha\beta}/r^6 \qquad (1)$$

where Q_α is the ionic charge on ion species α, and the first term describes the coulombic interaction between ions. The total force on a given particle is calculated by an Ewald summation procedure which takes account of long-range interactions and the periodic boundary conditions [8]. The essence of an MD simulation is then that Newton's equations of motion are solved simultaneously for each particle in the box by a numerical integration procedure. The method is rife with computational pitfalls but, if used judiciously, will result in a simulated 'life history' over a limited time-interval for each particle in the system.

This procedure provides us with a wealth of information regarding the structural and dynamical behaviour of our system. Phenomena such as short-range order, correlation, phase transition mechanisms and particle jumps can be derived from a careful analysis. A particularly instructive device is to plot out the paths of various selected particles within the simulation box (the so-called particle trajectories). These can, in turn, be further superposed within a single crystallographic unit-cell for comparison with the structural average obtained from a conventional diffraction experiment (see later example).

Although the precise character of the MD calculation will vary greatly from case to case, a number of general points can be indicated:

(i) A reliable model must be available for the 'well behaved' ordered part of the structure. It should be stressed, however, that these atoms are also free to move during the simulation, and that no symmetry constraints are imposed on the solution of Newton's equations.

(ii) Appropriate atom–atom potentials must also exist for all atom-pairs which arise in the calculation. Reasonably satisfactory potentials already exist for the most commonly occurring ion-pairs, but severe difficulties can be experienced in simulating hydrogen-bonded interactions, or interatomic interactions involving a high degree of polarization or covalency.

(iii) Simulations involving supercells of complex structures can easily become mitigatingly large, even for the most powerful of computers. In such cases, care must be exercised in deciding how (if at all) the simulation box can be simplified, yet still retain its meaningfulness. There can be no general rule as to how large the simulation box should be. However, it must at least exceed the correlation length(s) characteristic of the structural ordering effects under study, if these are to be simulated successfully.

(iv) Similarly, the disordered minority part of the structure must be introduced in an intelligent way. Typically, for a non-stoichiometric situation, several start configurations must be tested to check the generality of the final results.

(v) By the same token, regular checks are mandatory of the thermal equilibrium of the simulated structure. In this context, it is important that sufficiently many and sufficiently short time-steps are used.

AN EXAMPLE: Na^+ β''-ALUMINA

The example we choose, Na^+ β''-alumina, is experimentally one of the most studied representatives of a class of materials known generally as solid electrolytes. The most characteristic feature of this structure is the exceptionally high mobility of its Na^+ ions. These occupy an essentially two-dimensional conduction plane, separated by ≈ 11 Å thick spinel blocks. (The structure is rhombohedral, $R\bar{3}m$, with hexagonal axes: a ≈ 5.6 Å and c ≈ 33.8 Å; see schematic representation in Fig. 1). The structure has the ideal formula: $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$; substitution of Al^{3+} by Mg^{2+} at the centre of the spinel blocks serves as the charge compensation mechanism needed to allow extra Na^+ ions to be incorporated into the conduction plane, which otherwise contains only the so-called column oxygen O(5). Intrinsic non-stoichiometry is thus a critical structural feature (see later), with roughly five out of six of the Na^+ sites (BR-sites) occupied. Conventional diffraction analysis results in the time- and space-averaged Na^+ ion distribution in the conduction plane. Even after lowering the effective local space-group symmetry for the Na^+ ions [11, 12], the final distribution still lacks detailed information concerning local ordering processes (Fig. 2).
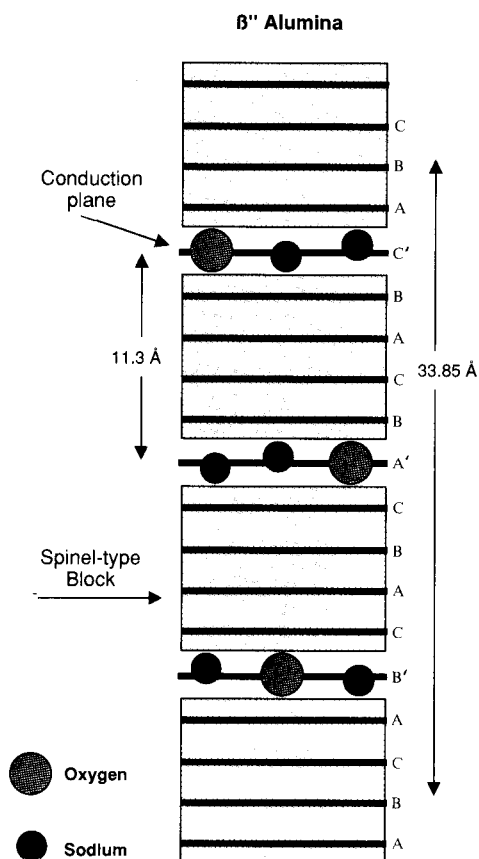
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Fig. 1. A schematic representation of the Na$^+$ β''-alumina structure. Solid lines marked A, B and C indicate layers of close-packed oxygen atoms belonging to the spinel blocks; solid lines marked A', B' and C' mark the three conduction planes per unit-cell.

Limitations in our computational capabilities have meant that certain compromises have been necessary in our MD treatment. A simulation box was used which extended outward, on either side of the conduction plane, as far as the centre of the spinel block, i.e. to the layer containing the O(1) and O(2) oxygens. All ions within a 4×3 unit-cell box of this thickness were free to move during the simulation under the forces they experience from all other ions; the O(1) and O(2) oxygens were fixed.

The remainder of the crystallographic unit-cell was 'empty'. This involved, in all, 20 Na$^+$ ions in the simulation box, along with four vacancies (Fig. 3). It should be noted that no account was here taken of Mg^{2+} substitution. Several different starting configurations were used for the Na$^+$ ions, to ensure that the final results were independent of starting conditions. A total of 1000 time-steps were normally calculated (each of 5×10^{-15} s) for each temperature after equilibration. The constants A, γ and C in Eq. (1) were the values given by Walker and Catlow [13] in their earlier simulations of the β- and β''-aluminas. The MD program used is a local modification of their program FUNGUS [14].
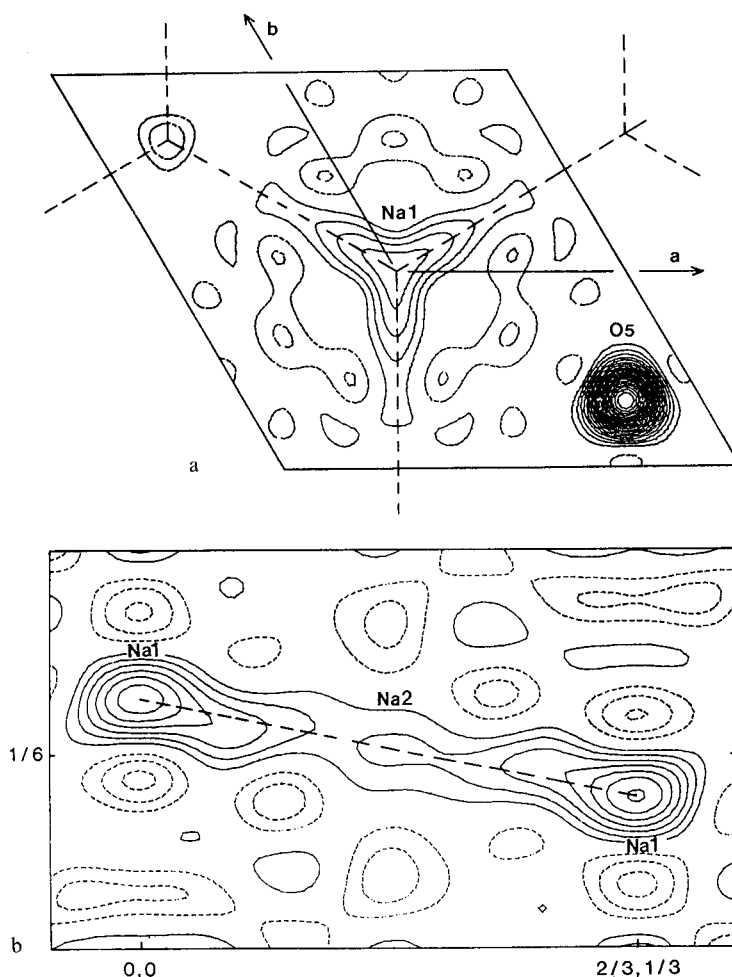
Fig. 2. Observed Na$^+$ ion distribution at 295 K in Na$^+$ β''-alumina, obtained from a single-crystal neutron diffraction study [11]. The sections (plotted with an arbitrary contour interval) are taken in the z = 0.172 plane (a), and in the (2x,x,z)-plane through the conduction pathway (b).

Since our purpose here is simply to demonstrate the use of MD simulation as a complementary crystallographic tool, we will only give some examples of the type of information the treatment provides, and not indulge ourselves too deeply in discussing the broader implications of the results presented.

(a) Na$^+$ distribution

Simulated trajectories for Na$^+$ and O(5) at four temperatures are plotted in projection in Figs. 4a–d. It can be noted how the mobility of the Na$^+$ ions increases dramatically with temperature – the first jump between adjacent BR-sites occurs at around 400 K – whereas the column-oxygens O(5) undergo normal vibrational behaviour. It is also noteworthy that the general appearance of the corresponding 'superposed' simulations (Figs. 5a–d) changes systematically with temperature.
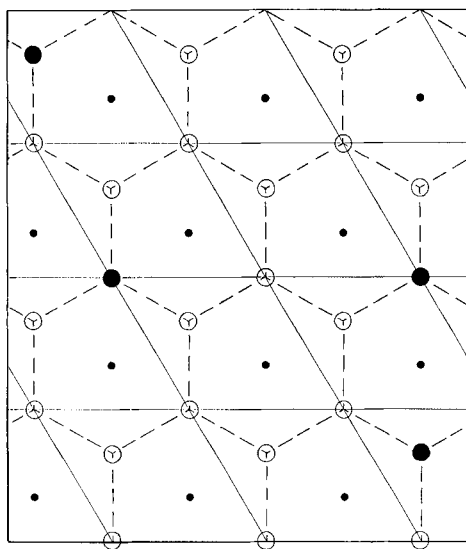
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Fig. 3. One of the start configurations used for the conduction plane of the simulation box. Small solid circles: O(5) column oxygens; large open circles: Na^+ ions at BR-sites; large solid circles: vacancies.

At lower temperatures, the superposition of the trajectories simulated within the 12-cell box looks radically different at the two BR-sites: Na^+ ions collect at one of the BR-sites, while they group at three off-centre positions around the second BR-site. Some suggestion of this effect was even detected when the experimental Na^+ distribution was refined within the non-centrosymmetric space-group R3m [11,12]. The MD simulation shows that this behaviour is merely a result of relaxation of Na^+ ions towards vacant BR-sites.

(b) Radial distribution functions (rdf's)

The structures of liquids and amorphous solids are generally expressed in terms of a radial distribution function. It is therefore of interest to enquire as to the form of the corresponding rdf for the mobile Na^+ ions in the present case. In Fig. 6, we plot the simulated Na^+-Na^+ rdf at 250 K and 800 K. We note that the loss of local order in the Na^+ sublattice, and the accompanying onset of Na^+ ion mobility are marked by some distinctive features: the peaks are seen to shift and the third peak at 7.8 Å ($= 1.38$ a) in the 250 K rdf has disappeared entirely at 800 K. It can be mentioned in this connection that Na^+ β''-alumina becomes 'superionically conducting' at around 500 K.

(c) Correlation effects

Careful inelastic neutron scattering experiments can, in principle, be used to detect correlation phenomena in mobile-ion systems. Generally speaking, however, one is hard-pressed to observe such effects experimentally. Analysis of the results of an MD simulation can thus provide valuable information in this connection. Inspection of our simulation of the Na^+ β''-alumina system has revealed an intriguing feature involving correlated ion motion: around 700 K, a dynamical superlat-
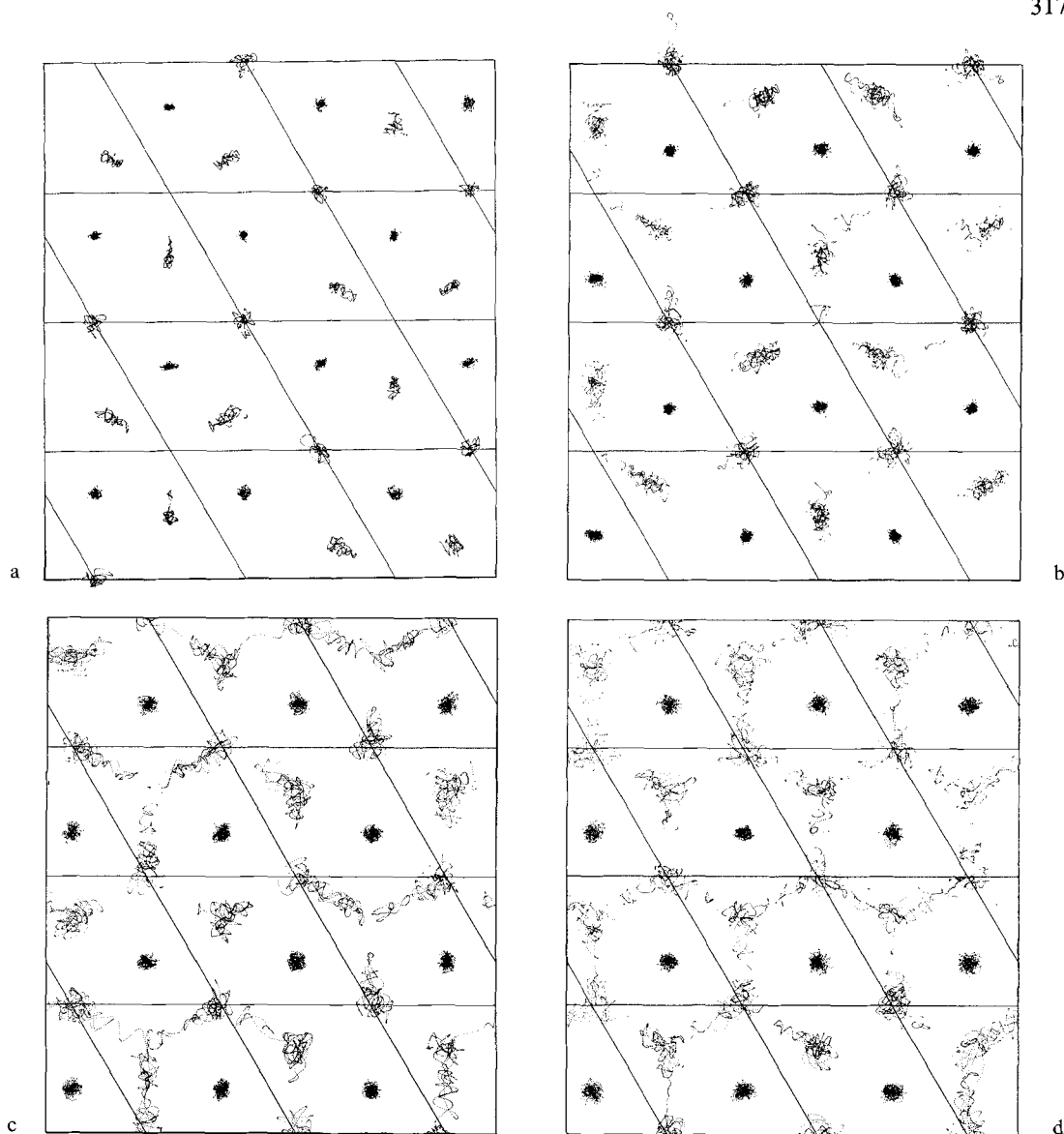
Fig. 4. Projected trajectories in a 4 × 3 simulation box at 250 K(a), 400 K(b), 650 K(c) and 800 K(d), showing the behaviour of the Na$^+$ ions and the O(5) column oxygens (1000 time-steps, each of 5 × 10^{-15} s).

tice emerges in which Na$^+$ ions move in rosette-like pathways around immobilized Na$^+$ ions, which themselves lie on a $\sqrt{3}$a × $\sqrt{3}$a superlattice. It remains to be seen whether this uniquely interesting behaviour is preserved in calculations made with a larger simulation box.

(d) Comparison with experiment

Clearly, projected trajectories cannot be compared quantitatively with the 3D distributions derived from a diffraction experiment. Taking an example: Fig. 2b shows a section taken through
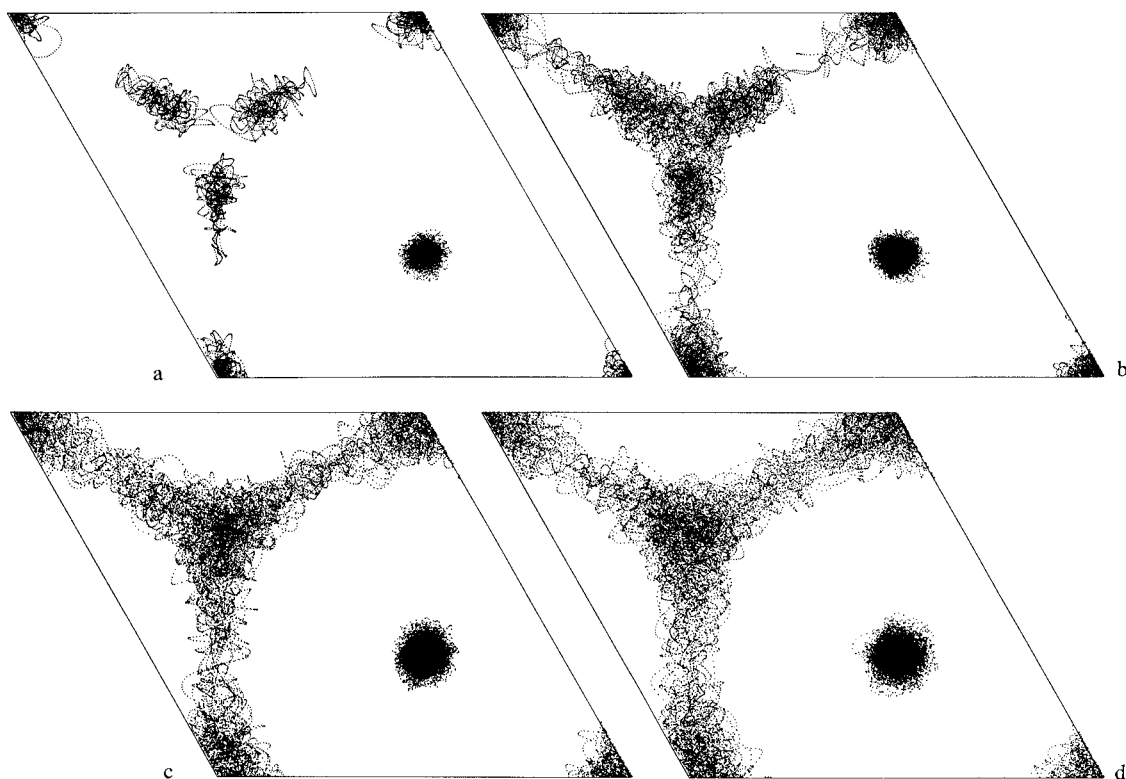
Fig. 5. Same plots as shown in Figs. 4a-d but superposed onto a single cell.

the neutron-diffraction determined Na^+ ion conduction pathway at 295 K, viewed perpendicular to the unique c-axis. A corresponding simulated section is prepared by selecting the set of simulated points within a 0.1 Å thick slice parallel to the c-axis (Fig. 8a); the projection perpendicular to this slice is then plotted in Fig. 8b. The resulting plot indeed bears some qualitative resemblance to the experimental distribution shown in Fig. 2b; notably, in the different character of the two BR-sites, and in the undulation in the Na^+ distribution in the conduction plane.

(e) Thermal analysis

An obviously rewarding application of MD methods is the analysis of thermal vibrations in solids. The standard crystallographic approach is again inadequate in resolving subtle detail in vibrational behaviour, e.g. individual modes, anharmonicity, local correlation effects, etc. The region occupied by a given scattering centre undergoing thermal motion is described by a set of so-called thermal parameters. These are refined as tensor terms in reciprocal space, from which the 3D time- and space-averaged atomic distribution (the probability density function, or pdf) can be derived. This is often represented graphically, within the harmonic approxiation, as a 50% probability ellipsoid. Spurious numerical correlations arise in the least-squares refinement procedure, however, between the various thermal, bonding and disorder parameters. Superposition of the MD simulated trajectories for each cell within some appropriate time interval allows us to
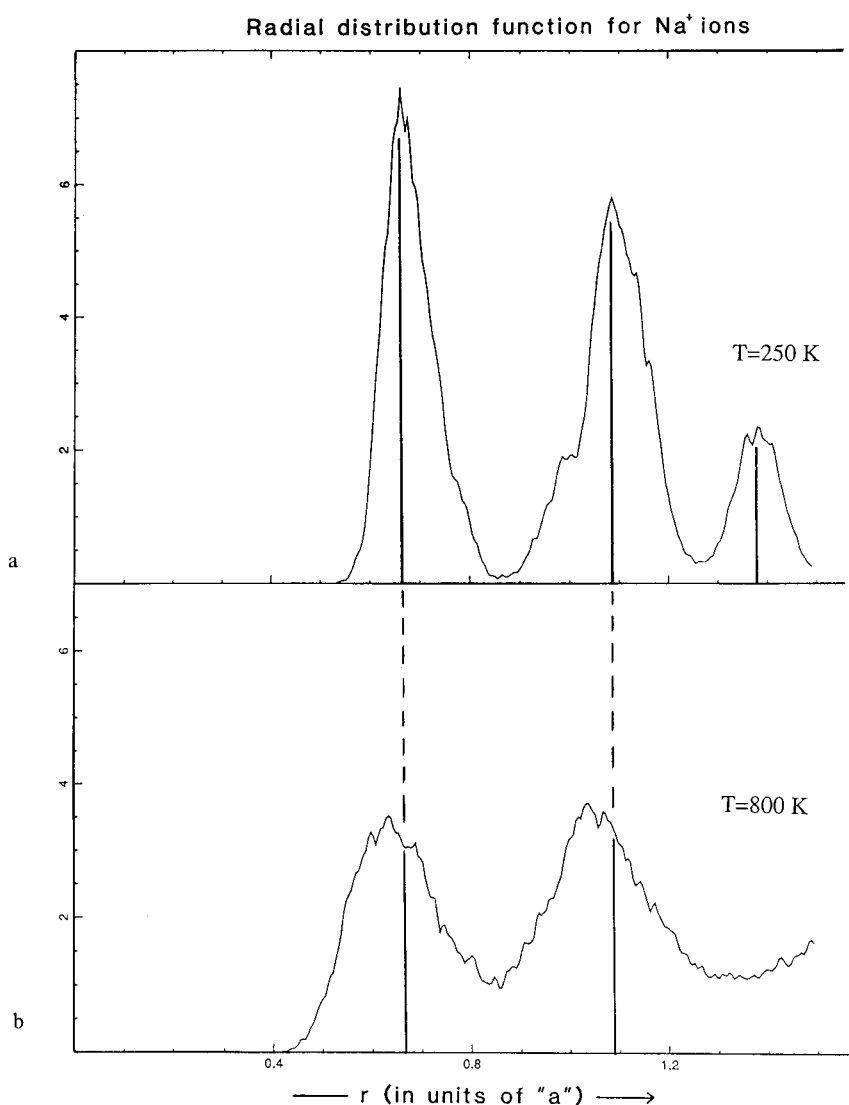
Radial distribution function for Na⁺ ions

Fig. 6. The Na⁺-Na⁺ radial distribution function (rdf) calculated from the MD simulation at 250 K and 800 K.

construct an ensemble of points related directly to the pdf's for the atoms in question. An example is given in Fig. 9 for the column oxygen O(5). The superposed points are plotted in and perpendicular to the conduction plane (Figs. 9a–b); the pdf for a central slice parallel to the conduction plane (the ab-plane) is given in Fig. 9c. Evidence of distinct thermal vibrational anisotropy is seen in Fig. 9a: the ratio between the half-widths of the in- and out-of-plane MD-derived pdf's is 2.5, compared with the experimentally observed ratio of rms vibrational amplitudes at 295 K of 3.9. This disagreement can be partly a result of some mismatch between the calculated and effective temperature of the simulation. The effect of systematic errors on the experimental thermal parameters (typically; systematically low β_{33}-values) can also contribute. It is reassuring to
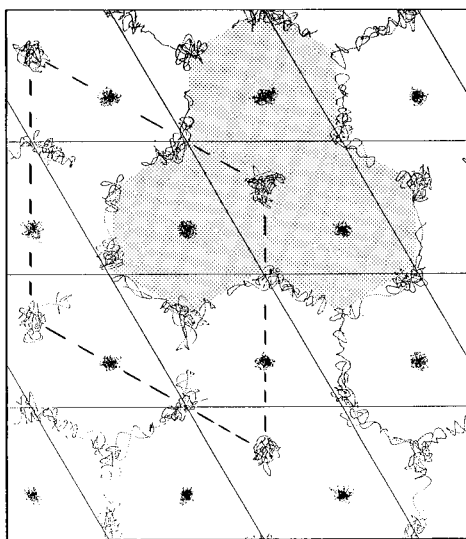
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Fig. 7. Simulated trajectories in the 4×3 cell at 700 K. Correlated jump motion around fixed Na^+ ions lying on a $\sqrt{3}a \times \sqrt{3}a$ superlattice is indicated by shading.

note, however, that MD simulation confirms the absence of disorder in the O(5) distribution in Na^+ β''-alumina, as indicated by the diffraction experiment. Such structural disorder is otherwise common in the β''-aluminas, especially when small multivalent cations are exchanged into the conduction plane.

(f) Effect of non-stoichiometry

Na^+ β''-alumina is an extreme case of a defect system in which the special property of the material, its exceptional Na^+ mobility, is a direct result of the high degree of non-stoichiometry in the system. The critical importance of non-stoichiometry can be illustrated most conveniently by an
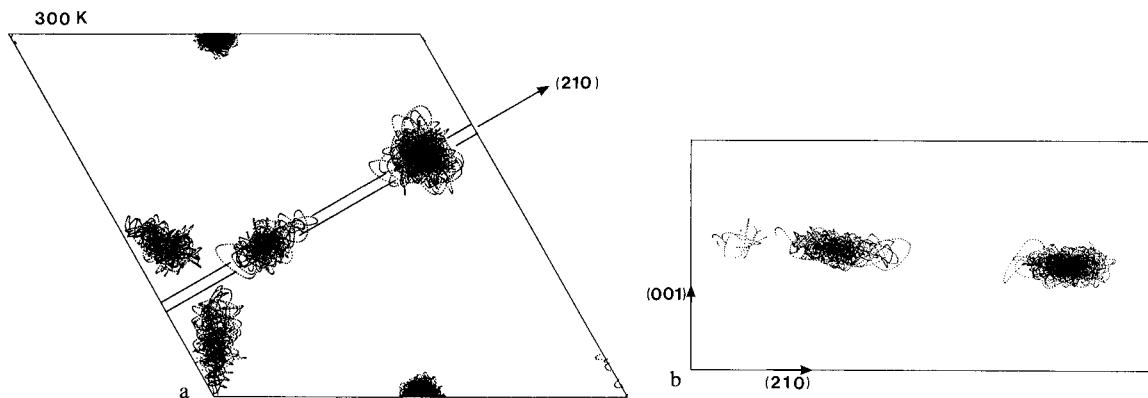

Fig. 8. Illustration of the method of preparation of a plot comparable with the experimental density in Fig. 2b. The points contained within the 0.1 Å slice parallel to the z-axis indicated in (a) are viewed in projection in (b).

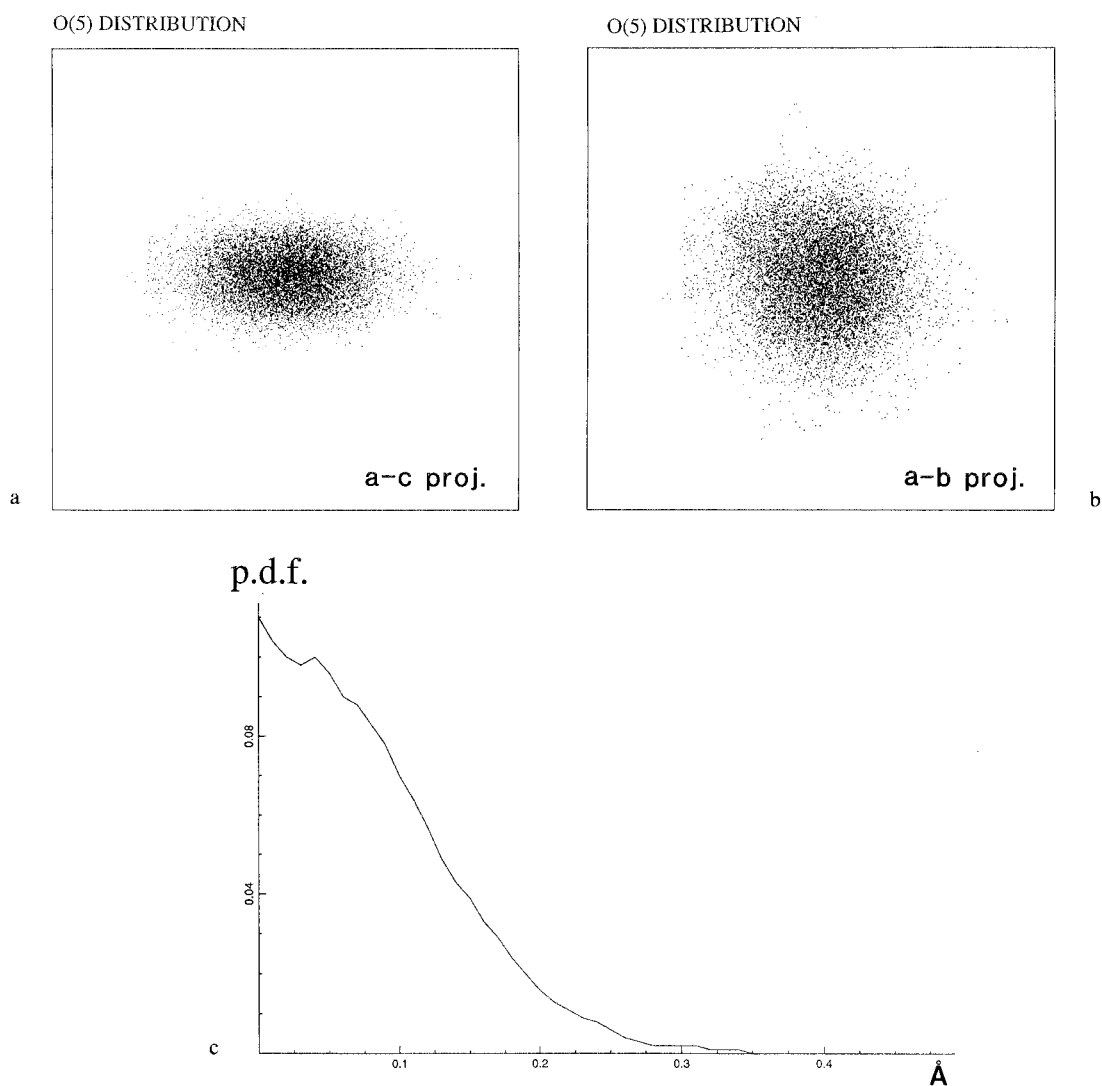O(5) DISTRIBUTION

O(5) DISTRIBUTION

Fig. 9. A projection of the superposed simulated points representing column oxygen O(5) parallel (a) and perpendicular (b) to the conduction plane. The pdf for the points in (a) which are contained within a central 0.1 Å slice are plotted in (c), cf. Fig. 8.

MD simulation of the hypothetical stoichiometric compound $Na_2MgAl_{10}O_{11}$, in which all 24 BR-sites are occupied in the 4×3 simulation box. Figs. 10a–f summarize the simulation at 500 K and 1200 K. We can note that, even at the higher temperature, the normally mobile Na^+ ions continue to vibrate about their crystallographically ideal positions. Even the fine-structure of the corresponding rdf is maintained. This application of MD simulation further serves to underscore its pedagogic value.
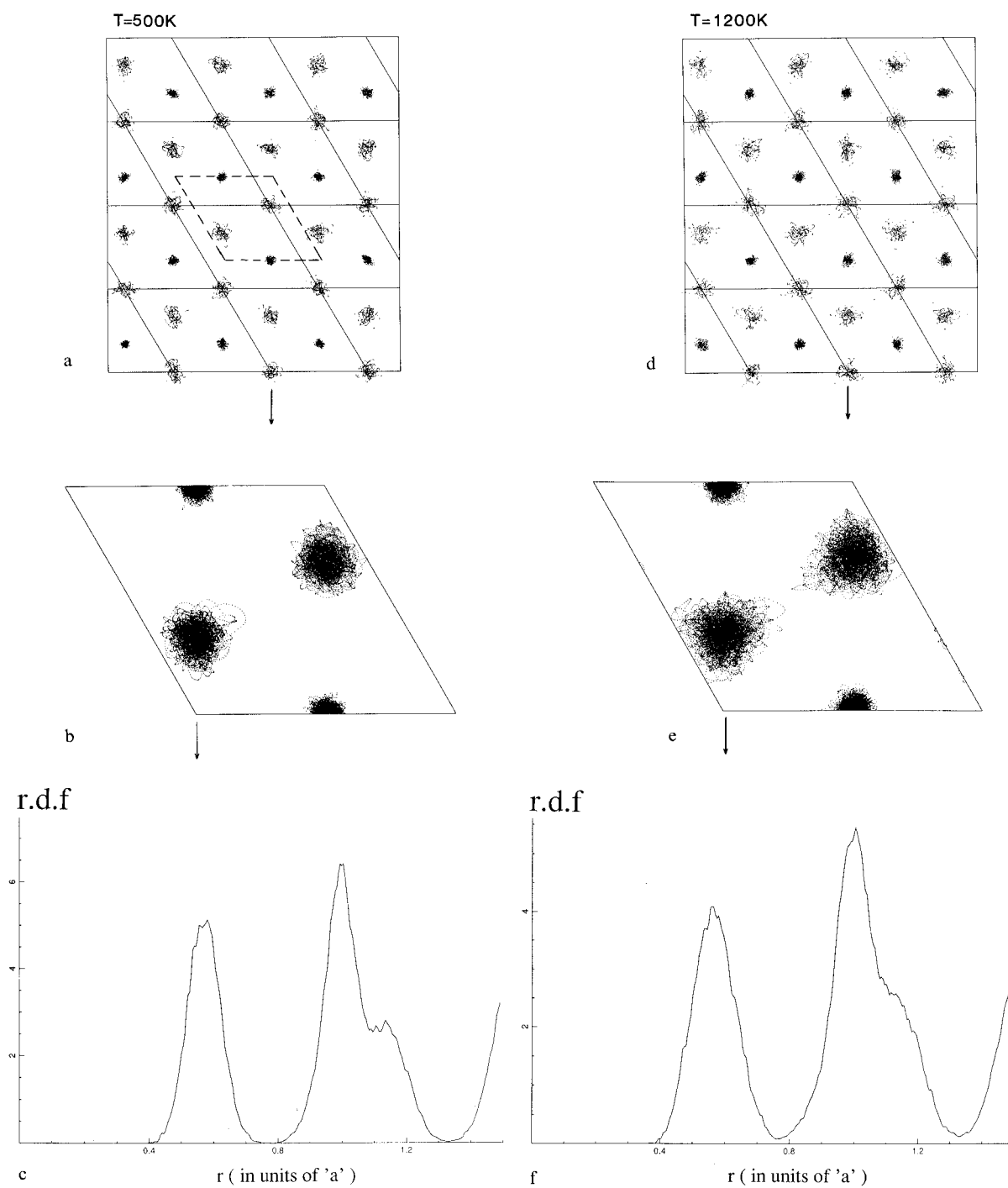
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T=500K

T=1200K

a

d

b

e

r.d.f

r.d.f

c

r (in units of 'a')

f

r (in units of 'a')

Fig. 10. The trajectories, superposed cells and corresponding rdf's at 500 K(a–c) and 1200 K(d–f) for the hypothetical case of stoichiometric Na^+ β''-alumina.
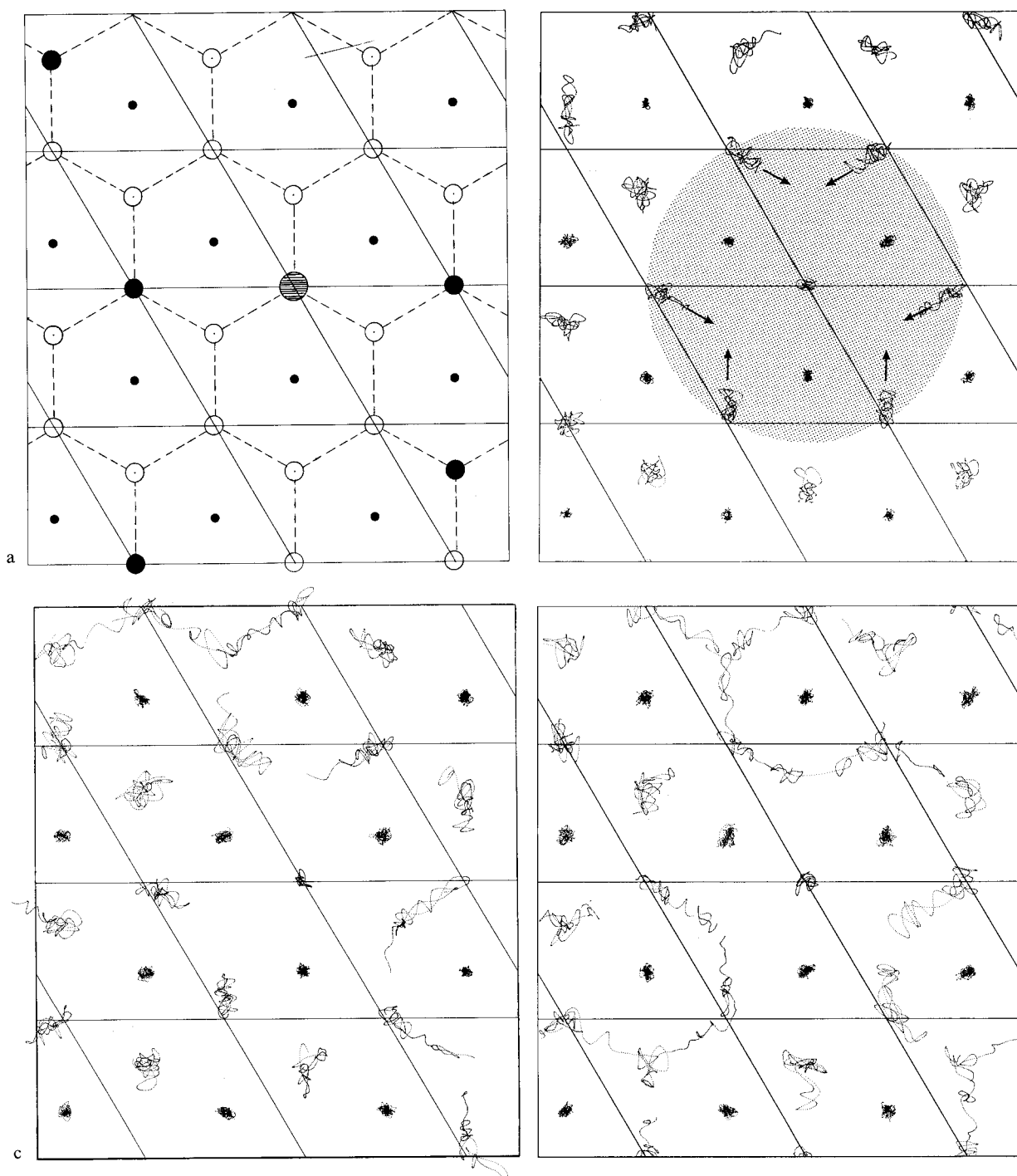
Fig. 11. MD simulation of the mixed-ion compound Na$^+$/Ba^{2+} β''-alumina. (a) The start configuration. Small solid circles: O(5) column oxygens; large open circles: Na$^+$ ions at BR-sites; large shaded circle: Ba^{2+} ion at a BR-site; large solid circles: vacancies. The simulated trajectories in the 4×3 cell are plotted at 300 K(b), 550 K(c) and 800 K(d). The cluster is represented as the shaded area in (b).

(g) Mixed-ion systems

Finally, we would like to illustrate the predictive usefulness of MD simulation in situations where experimental methods are, for one reason or another, inadequate. A typical example is a mixed-ion system, where two or more ion-types can 'overlap' on crystallographically equivalent sites. In as much as each ion retains its identity in an MD treatment, the power of the method lies in that it allows us to isolate local ordering processes in an experimentally unresolvable situation. We illustrate this for the case of a Ba^{2+} ion substituted into the Na^+ β''-alumina conduction plane. Both Na^+ and Ba^{2+} ions tend to occupy BR-sites [7] and, in Fig. 11, we show a sequence of simulations of a 4×3 cell in which two of the 20 Na^+ ions have been replaced by one Ba^{2+} ion (Fig. 11a). The trajectories first show how a local structurized cluster forms around the Ba^{2+} ion at 300 K (Fig. 11b). The cluster comprises three nearest-neighbour BR-site vacancies, and six next-nearest neighbour Na^+ ions relax towards these vacancies. This configuration must seriously limit the pathways available for Na^+ mobility, and affect the ionic conductivity accordingly. As the temperature is increased, we observe that the cluster has begun to break up by 550 K (Fig. 11c), and has already disappeared at 800 K (Fig 11d). Molecular dynamics thus provides a delightful intuitive understanding of the mechanism whereby the introduction of a divalent ion into the Na^+ β''-alumina conduction plane could bring about a reduction in conductivity.

CONCLUSIONS

The molecular dynamics technique has been used to probe local structural order in the highly defective fast-ion conductor Na^+ β''-alumina. A detailed analysis of ionic distribution at different temperatures is presented, along with corresponding diffraction-determined distributions. It is seen how intimately the two techniques can complement one another. In addition, a number of features have emerged from the MD treatment: the crucial role of non-stoichiometry in determining ion mobility, dynamical superlattice formation over a limited temperature range, as well as the uniquely interesting cluster formation around the Ba^{2+} ion in Na^+/Ba^{2+} β''-alumina. The latter phenomenon can be of great importance in understanding transport properties in mixed-ion systems. Note, however, that MD techniques in general, and our calculation in particular, can produce results which subsequently prove to be incorrect, typically through the use of inappropriate ion–ion potentials. This must be seen as an ever present problem in MD work, and one which needs much attention in the future.

ACKNOWLEDGEMENTS

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