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A molecular dynamic simulation of gadolinium-doped SrF₂

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Abstract. Molecular dynamic simulations of SrF₂ doped with 0.9 and 9.0 mol% Gd at an effective temperature of $T = 0.9T_m$ show that the dominant mode of ionic transport is in the $\langle 001 \rangle$ directions, as in the pure fluorite. Extensive clusters of vacancies and interstitials, such as the 2:2:2 cluster were not observed although features of the quasi-elastic neutron scattering—indicating the presence of discrete clusters—were reproduced; their presence was also supported by the relative concentrations of vacancies and interstitials. Several examples of short-lived linear crowdion clusters were observed and these simple clusters are consistent with the data presented here.

1. Introduction

Crystals with the fluorite structure have been favoured as pedagogical models for studying the properties of defective solids. These materials are able to accommodate as much as 30–40 mol% of aliovalent cation impurities, together with their charge compensators, in solid solution. The results are ideal systems in which it is possible to observe defect structures ranging from isolated impurities to complex defects, incorporating many impurities and charge compensators. The fluorite structure also happens to be one of the simplest which can support fast ionic motion. It consists of a cubic anion sublattice within which every other body-centred site is occupied by a cation. A large body of experimentally observed properties of the fluorites exists (see, e.g., Hayes 1974, Chadwick 1983). Also, neutron diffraction studies (Clausen *et al* 1981, Hutchings *et al* 1974, Dickens *et al* 1980) have provided direct evidence for the existence of discrete defect structures within these materials.

In SrF₂, ionic transport is achieved by the thermal generation of anion Frenkel defects. Doping this material with aliovalent impurities such as Gd³⁺ in a reducing atmosphere results in the incorporation of additional anion interstitials as charge-compensating elements. At low impurity concentrations, where the impurity cations are isolated from one another, the anion interstitials may sit at sites of tetragonal or trigonal symmetry with respect to the impurity, or the cation and interstitial may be dissociated. At higher impurity concentrations, discrete clusters of impurity ions and interstitials may be formed (Catlow *et al* 1981, Corish *et al* 1982). The importance of these clusters

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to ionic transport lies in their ability to trap the thermally generated interstitial anions and the binding energy of the cluster so formed effects a reduction in the anion Frenkel energy. This reduction lowers the transition temperature to the fast-ion regime.

Although strong experimental evidence for the existence of clusters has been accumulated, molecular dynamic simulations of the fluorites (Mościński and Jacobs 1985, Gillan and Dixon 1980a) have uniformly failed to detect the existence of any clustering. One explanation put forward (Catlow and Hayes 1982) is that even simple clusters occupy volumes of about $3.5a_0^3$, where a_0 is the lattice constant, which is significant when compared with the volume of the simulation of $27a_0^3$. However, Gillan and Dixon (1980b) found that a small-sized simulation of volume $8a_0^3$ was able to reproduce the experimentally observed features of the neutron diffraction data which had been ascribed to the existence of clusters. This discrepancy remains to be resolved. The purpose of the present work is to report two molecular dynamic simulations of SrF_2 doped with aliovalent Gd at a low and a high concentration. The presence of impurities increases the probability of stable cluster formation; this simulation of the material shows a good chance of observing cluster formation which otherwise might require very lengthy calculations. We also comment on the mechanism of ionic transport in doped materials and compare them with the pure fluorite. The numerical calculations reported here were performed in 1985 during the tenure of a Commonwealth Scientific and Industrial Research Organisation Oversea Fellowship held by one of us (DB) and the analyses were made at a later date.

2. Defects

Three types of simple fluoride ion defect, shown in figure 1, are identified for the present work:

- (i) anion vacancies at regular anion sites;
- (ii) anion interstitials located at the body centre position of the anion cube;
- (iii) anion interstitials located directly between two regular anion sites (the cube edge site), which would normally be occupied by anions migrating in the $[100]$ directions.

Additionally, more extensive defect structures have been postulated, involving vacancies, interstitial ions and ions relaxed from their regular ion sites. Extensive investigations, both experimental (see, e.g., Hutchings *et al* 1984) and theoretical (see, e.g., Catlow and Hayes 1982) have been performed in order to elucidate the nature of clustering in the fluorites. The cluster type that has attracted significant attention is one with two interstitial anions accompanied by relaxation of neighbouring anions: this is the 2:2:2 cluster ($2|2_1$ in the notation of Corish *et al* (1982)). The cluster may be stabilised either by anion vacancies (Catlow and Hayes 1982) or by trivalent impurities, as shown in figure 1(c) (Catlow 1973). Many other cluster types have been proposed, among the more promising of which are crowdion clusters (Hutchings *et al* 1984) in which all the displaced anions were originally located on the same $\langle 100 \rangle$ axis, and clusters formed from crowdions, with additional relaxation of neighbouring anions. The simplest crowdion cluster, 3:1:2, consisting of three vacancies, one interstitial and two relaxed anions, is shown in figure 1(d). One of the primary objectives of the present work is the identification of clusters, if formed, during the molecular dynamic simulation. Previous simulations (Mościński and Jacobs 1985, Gillan and Dixon 1980a, b, Dixon and Gillan 1980) have failed to provide any evidence for the existence of clusters.

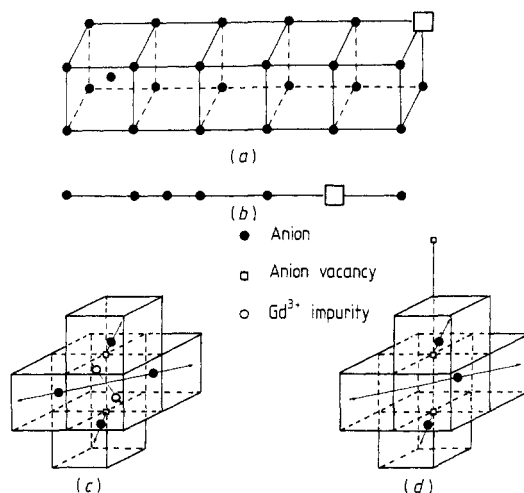


Figure 1. Schematic representation of simple defect clusters: (a) vacancy at a regular anion site and an anion interstitial at the cube centre position; (b) simple linear crowdion with the interstitial midway between two anion sites; (c) the 2:2:2 cluster stabilised by two trivalent impurities; (d) the 3:1:2 cluster containing one true interstitial and two relaxed anions.

3. The simulation

A primary box of side length three lattice constants was used, together with periodic boundary conditions, to extend the crystal lattice to infinite distances. For pure SrF₂, the primary box contained 324 ions (108 cations and 216 anions). The effects of isolated impurities and impurity interactions were explored by performing two simulations; the first was at a low impurity concentration, where one Sr²⁺ ion was replaced by a trivalent Gd³⁺ ion. This resulted in a dopant concentration of 0.9 mol% and an impurity–impurity separation of $3a_0$ —large enough that the Gd³⁺ ions may be considered to be isolated. In order to maintain electrical neutrality, a compensating fluoride ion was added to the simulation. In the second simulation, 10 Sr²⁺ ions were replaced by Gd³⁺ ions and 10 F⁻ ions were added to give a dopant concentration that was an order of magnitude larger than the first. At this impurity level, we expect that the Gd³⁺ ions are not isolated from each other. The impurity ions were added to the simulation in a random way and in all cases the charge compensation F⁻ ions were added at cube-centred interstitial sites.

For the details of the molecular dynamic technique we refer to the extensive reviews that may now be found in the literature (see, e.g., Catlow and Mackrodt 1982, Sangster and Dixon 1976). A time step of 10^{-14} s was chosen; this is an order of magnitude smaller than the shortest vibrational period in these materials (Gillan and Dixon 1980a). Equipartitioning of the kinetic and potential energies was used to expedite the equilibration process.

Both simulations were performed at a nominal temperature of $T = 1700$ K which is near the experimentally observed melting temperature T_m of SrF₂ of 1723 K. However, in an accompanying paper (Bingham *et al* 1989, hereafter referred to as I), it was found from a 96-ion simulation of pure SrF₂ that the simulated melting temperature is $T_m(\text{simulation}) = 1850 \pm 50$ K. On rescaling to this temperature, we find the simulation temperature to be $T = 0.9T_m$. This is intermediate between the transition to the fast-ion

transport regime $T_c = 1400$ K (Chadwick 1983) and the melting point, since $T_c = 0.8T_m$. The lattice constant used for the simulations was $a_0 = 0.6095$ nm (I).

4. Diffusion coefficients

The anion diffusion coefficients D may be calculated from the mean-square fluoride ion displacements $\langle r^2(t) \rangle$ (Einstein 1905) as a function of time t :

$$\langle r^2(t) \rangle = 6D|t| + B$$

where B is a constant term. Using the Nernst–Einstein equation and the appropriate correlation factor (I), we deduce the ionic conductivity as $\log \sigma = 2.18 \pm 0.02 \Omega^{-1} \text{m}^{-1}$ and $\log \sigma = 2.27 \pm 0.02 \Omega^{-1} \text{m}^{-1}$ for Gd^{3+} ion concentrations of 0.9 mol% and 9.0 mol%, respectively.

The derived conductivity at the lower Gd^{3+} ion concentration is in excellent agreement with that obtained from a smaller 96-ion simulation (I) while the increase in the conductivity at higher dopant concentration is in accord with the experimentally observed trend (Chadwick 1983).

For both simulations, the cation diffusion coefficient was negligible, indicating that the simulated material is below its melting point.

5. Quasi-elastic neutron scattering

Experimental evidence for the existence of clusters in fluorites at temperatures above T_c , i.e. $T \approx 0.9T_m$, has mainly been obtained from quasi-elastic neutron scattering. The materials SrCl_2 , PbF_2 , CaF_2 and BaF_2 show the existence of a quasi-elastic peak, centred at zero energy, the intensity of which has a pronounced dependence on the wavevector (Hutchings *et al* 1984, Dickens *et al* 1978, Dickens *et al* 1980, Clausen *et al* 1981). For these materials, the distribution of scattering intensity is similar, and the peak widths are in the range 0.5–2 meV, corresponding to lifetimes τ of about 10^{-12} s. The quasi-elastic scattering has been interpreted as evidence for the existence of transient clusters of displaced anions with a well defined structure that is not simply related to the lattice (Catlow and Hayes 1982).

A molecular dynamic simulation of SrCl_2 (Gillan and Dixon 1980b) using 96 ions was able to reproduce the experimentally observed appearance of the quasi-elastic scattering peak for temperatures $T > T_c$, although a detailed examination of the anion motions was not made.

An accurate calculation of the quasi-elastic scattering requires both short time steps and a very lengthy calculation. As such, this present work is not suitable for an extensive calculation of this quantity. Consequently, we have restricted ourselves to confirming the presence of the quasi-elastic scattering near $\mathbf{k} = (\frac{2}{3}, 0, 0)$ close to a region of high intensity. The results of the two Gd^{3+} ion concentrations are shown in figure 2. The general features of the calculated scattering at a low concentration are similar to that calculated by Gillan and Dixon (1980b); thus we might expect that the mechanism responsible for the existence of the quasi-elastic peak is present in both systems. The quasi-elastic peak is not as apparent for 9.0 mol% Gd^{3+} (see figure 2(b)) and we discuss this feature later.

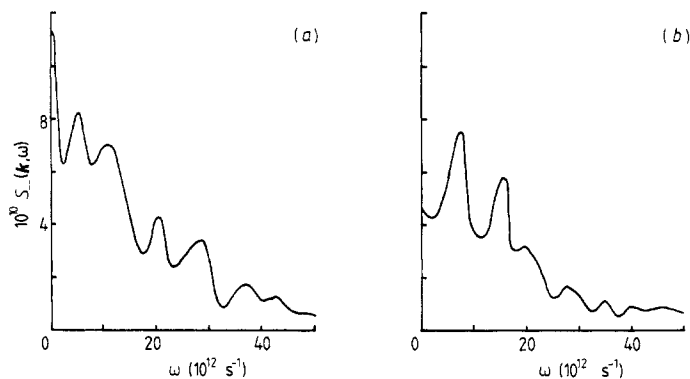


Figure 2. Partial dynamic structure factor $S(k, \omega)$ at $k = (2\pi/a_0)(\frac{1}{3}, 0, 0)$ at $T = 1700$ K for a Gd concentration of (a) 0.9 mol% Gd and (b) 9.0 mol% Gd.

6. Defect lifetimes

The catalogues of ion positions resulting from the molecular dynamic simulations were used to extract the distributions of lifetimes of simple defects: vacancies, cube centre interstitial anions and cube edge interstitial anions. These are shown in figure 3 for 0.9 mol% Gd^{3+} and 9.0 mol% Gd^{3+} , respectively. The lifetimes were extracted by tabulation of the times for which the particular sites were unoccupied (occupied). A site was deemed to be unoccupied (or occupied) if an anion was not (or was) found within a sphere of radius r , centred at the nominal site position. The lifetimes of cube edge interstitials were formed from the length of time that the anions were not at regular or body centre sites. As such, the concentration of this defect may be overestimated since a small volume of space in the (111) direction is included in the definition. Two radii were chosen, $r = 0.17a_0$ and $r = 0.21a_0$. In figure 3, the results for the latter radius, where calculated, are shown as a broken curve.

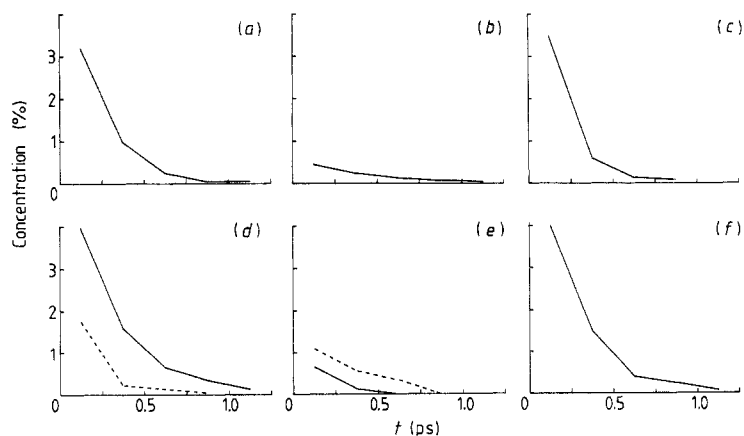


Figure 3. Lifetimes of simple defects: (a) vacancy concentration of 0.9 mol.% Gd, (b) cube centre interstitial of 0.9 mol.% Gd, (c) cube edge interstitial concentration of 0.9 mol.% Gd, (d) vacancy concentration of 9.0 mol.% Gd, (e) cube centre interstitial concentration of 9.0 mol.% Gd and (f) cube edge interstitial concentration of 9.0 mol.% Gd.

The magnitude of the observed vacancy concentration of 3–4% with lifetimes of 0.5 ps or longer is in good agreement with that derived from neutron diffraction data in isostructural materials for the number of true Frenkel defects (Hutchings *et al* 1984) at T_c , i.e. 3–8% for PbF_2 , 1–5% for SrCl_2 and 2–7% for CaF_2 . There is negligible occupation of the body centre site. At the temperature of the simulation the majority of vacancies are short lived and probably engaged in simple hops between near-neighbour sites, the transit time being of the order of 0.3 ps.

Unfortunately, the data, as presented, do not allow unambiguous determination of the mean cluster types, as derived from the concentration ratio of vacancies: interstitials: relaxed anions, although the ratio of vacancies: cube edge interstitials is approximately unity. This ratio favours the existence of the 2:2:2 and smaller crowdion clusters such as 3:1:2 over more extensive crowdions such as 9:1:8, where the vacancy: interstitial concentration differs by an order of magnitude albeit that the extra vacancies are formed through ion relaxations. The ion catalogues have been searched extensively for the existence of the 2:2:2 cluster but without success, however.

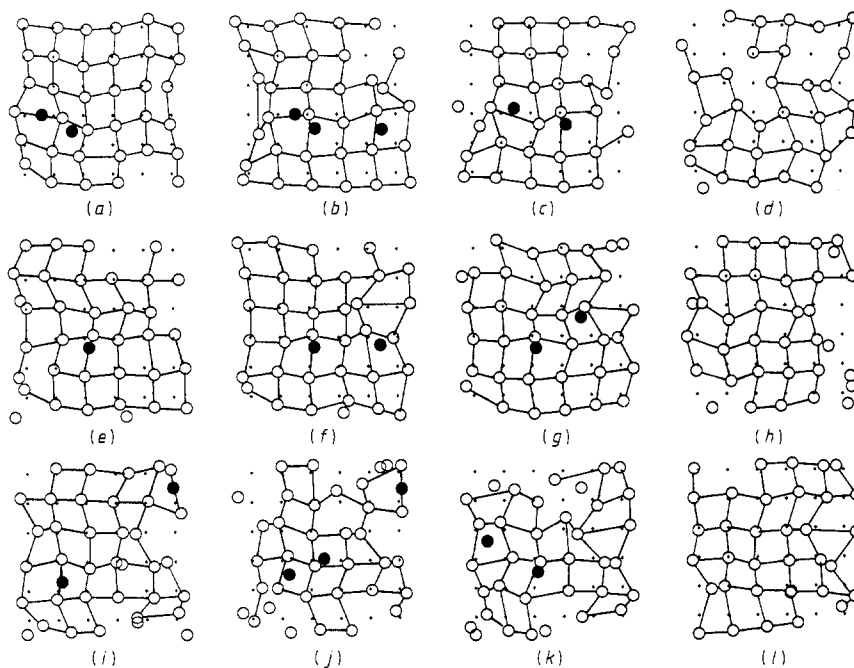


Figure 4. Time evolution of anion positions for 0.9 mol% Gd at a cross section of the simulation of $(0.0, -0.25 \pm 0.25)$. Each snapshot is averaged over 0.2 ps and time evolves across and down the figure. Interstitial ions are indicated as full circles. The long-lived interstitial in the lower left quadrant of most snapshots is bound to a Gd impurity. Examples of configurations consistent with linear crowdions appear in snapshots (b), (c), (i) and (j).

In figures 4 and 5 we show the time evolution of anion positions in a (001) plane over a period of 2.4 ps. For each snapshot the anion positions were averaged over 0.2 ps, and time evolves across and down each figure. This method of depiction was chosen, over others such as trajectory maps, in order to demonstrate the existence of any relatively long-lived ion configurations that might be consistent with the differing types of clusters

under consideration. Greatly increased disorder is evident at the higher Gd^{3+} concentration while there exist several examples of vacancies and interstitial anions which are consistent with the existence of linear crowdion clusters within the material. The lifetimes of these structures is in the order of 0.5 ps, a time scale which is consistent with that observed from the neutron scattering data. The interstitial anions are found to lie along the [001] axes or to be displaced from this direction.

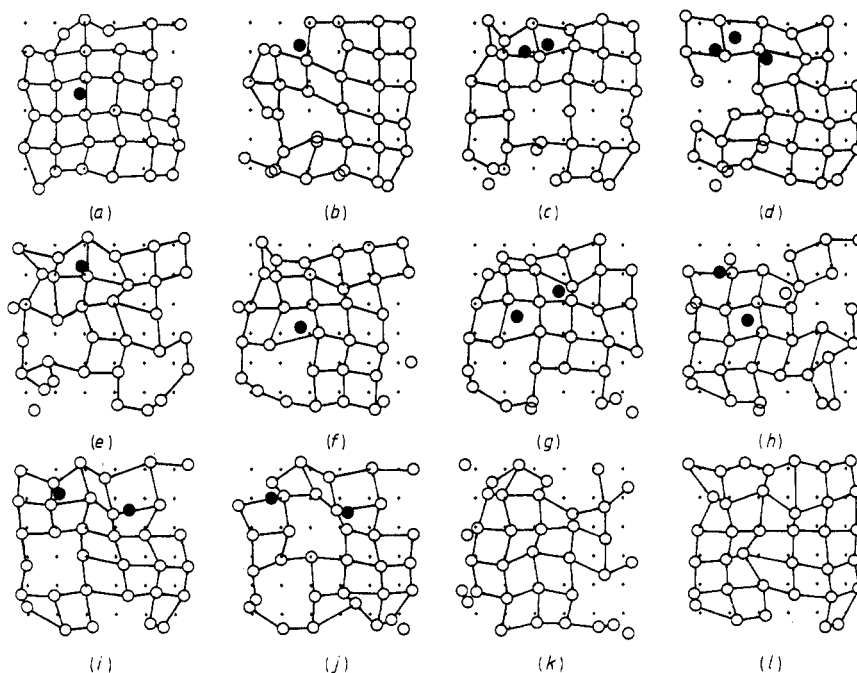


Figure 5. As for figure 4 but for 9.0 mol.% Gd and a cross section of $(0.0, 1.25 \pm 0.25)$. Examples of possible crowdions appear in snapshots (b), (c), (e), (f) and (g).

7. Radial distribution functions

The radial distribution functions (RDFs) for F^- ions with respect to Gd^{3+} and Sr^{2+} for both low and high impurity concentrations are shown in figure 6. The RDFs of Sr^{2+} with respect to Sr^{2+} ions exhibit maxima characteristic of solids and are similar to those presented elsewhere.

The F^- - Gd^{3+} RDFs for both low and high Gd^{3+} ion concentrations show the expected inward relaxation of the next-nearest neighbour F^- ion shell, when compared with the F^- - Sr^{2+} RDFs. In particular, the differing relaxations of this shell due to the presence of a tetragonally coordinated F^- interstitial ion can be seen for 0.9 mol% Gd^{3+} . At the higher Gd^{3+} ion concentration the greater degree of anion motion associated with the increased impurity concentration has the effect of blurring out this detail. There is no evidence for the presence of more than one F^- interstitial within a radius of $1a_0$ of the Gd^{3+} ions at low or high Gd^{3+} ion concentration. This interstitial lies along the [100] direction.

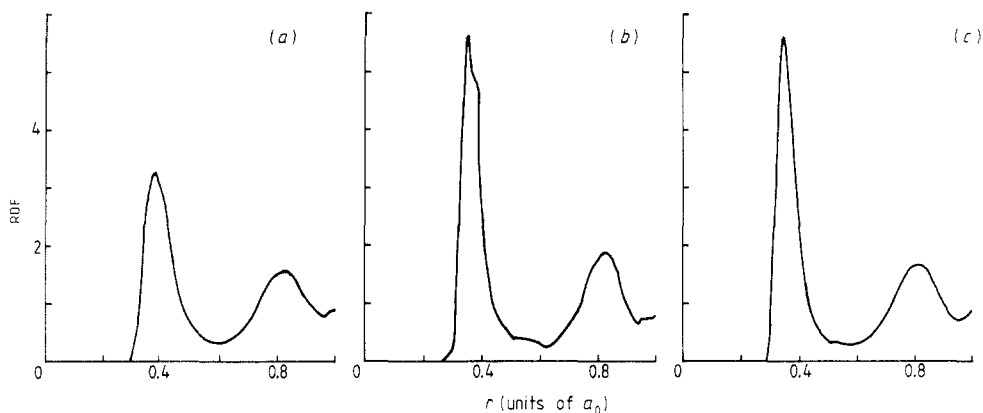


Figure 6. RDFs: (a) F^- with respect to Sr^{2+} (0.9 mol% Gd); (b) F^- with respect to Gd^{3+} (0.9 mol% Gd); (c) F^- with respect to Gd^{3+} (9.0 mol% Gd).

8. Effect of high Gd^{3+} ion concentration

The ionic conductivity is observed to rise by about 20% on increasing the Gd^{3+} ion concentration by an order of magnitude. Associated with this rise is a 50% increase in the total vacancy concentration and a 50% rise in the occupation of the cube edge interstitial site. There is no significant increase in the occupation of the body centre interstitial site. Since the increase in the conductivity is lower than might be expected from the increased vacancy concentration, it is evident that some trapping of thermally generated vacancies and interstitial ions occurs.

The RDFs for both low and high Gd^{3+} ion concentrations indicate the presence of a single charge-compensating interstitial within a radius of $1a_0$. This interstitial is in a site of tetragonal symmetry with respect to the Gd^{3+} ion impurity as determined from the site occupancies. At the higher Gd^{3+} ion concentration, there is no evidence from the RDFs that there is a significantly larger number of fluoride ions per unit volume within a radius of $1a_0$ of the Gd^{3+} ion impurity. Any trapping of thermally generated interstitials which occurs must then be over a volume greater than $4a_0^3$.

The particle trajectories exhibit a much greater degree of disturbance at high Gd^{3+} ion concentrations, which is evident in both the anion and the cation sublattices. This activity may be associated with the increased mass of the impurities and with the increased vacancy concentration; the averaged anion distribution around divalent cations remains unchanged.

9. Discussion

Despite an impressive degree of agreement between simulation and the experimental data that has developed as the simulation technique (as applied to the fluorites) has been progressively refined (Rahman 1976, Gillan and Dixon 1980a, Mościński and Jacobs 1985), the basic dichotomy between theory and experiment over the observance of clusters remains unresolved. Clusters have not been observed in any previous simulation and we have not made an unambiguous observation here.

However, we have been able to show that the mechanism responsible for the appear-

ance of the quasi-elastic neutron scattering peak found in the small-scale simulation of Gillan and Dixon (1980b) is also operative in the present work. An extensive search of the catalogue of ion positions has not revealed the presence of a 2:2:2 cluster, or indeed an approximation to this structure, but we have seen numerous examples of aggregates of ions with lifetimes of the order of 0.5 ps which are consistent with the existence of linear crowdions. Further, the existence of these structures is also consistent with the circumstantial evidence drawn from the site occupation and RDFs. It should be noted that the simulations were performed at a relatively high temperature ($T \approx 0.9T_m$) where it is expected that any other than strongly bound clusters will have lifetimes that are relatively short. In this circumstance, the greater relative stability of the 2:2:2 cluster with respect to linear crowdions is not relevant, and the degree of disturbance of the anion sublattice favours the generation of smaller simpler aggregates. It is highly probable that the 2:2:2 cluster is formed at lower temperatures and with longer lifetimes. While the above evidence is mainly inferential in nature, we have been able to demonstrate that the addition of aliovalent impurities does give rise to an increase in the vacancy concentration and that there is some trapping of thermally generated defects, which occurs at distances greater than $1a_0$. It is reasonable to expect that an effective reduction in the anion Frenkel energy results from this process and that there is a lowering of T_c , in accord with the experimental data (Chadwick 1983).

An explanation for the decrease in the calculated quasi-elastic scattering for an impurity concentration of 9.0 mol% Gd³⁺ is that the impurity ions form multiply connected structures of low symmetry. Defect structures formed within this network must necessarily be different from those formed at low concentrations and hence there is a decreased probability of forming the extended symmetric structures which are responsible for the quasi-elastic scattering.

Static defect calculations (I) performed with an increased lattice constant, in order to approximate the effect of elevated temperature, suggest that the trigonal charge compensation site becomes favoured over the tetragonal at high temperature. This reorientation, if it occurs, might be accommodated by a deviation of the F⁻ interstitial from $\langle 001 \rangle$ —although the magnitude of this deviation is not such as to be observable in the present analysis.

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References

- Bingham D, Cormack A N and Catlow C R A 1989 *J. Phys.: Condens. Matter* **1** 1205
- Catlow C R A 1973 *J. Phys. C: Solid State Phys.* **6** L64
- Catlow C R A, Comins J D, Germano F A, Hartley R T, Hayes W and Owen I B 1981 *J. Phys. C: Solid State Phys.* **14** 329
- Catlow C R A and Hayes W 1982 *J. Phys. C: Solid State Phys.* **15** L9
- Catlow C R A and Mackrodt W C (ed.) 1982 *Springer Lecture Notes in Physics* vol 166 (Berlin: Springer)
- Chadwick A V 1983 *Solid State Ion.* **8** 209

- Clausen K, Hayes W, Hutchings M T, Kjems J K, Schabel P and Smith C 1981 *Solid State Ion.* **5** 589
- Corish J, Catlow C R A, Jacobs P W M and Ong S H 1982 *Phys. Rev.* **B 25** 6425
- Dickens M H, Hayes W, Smith C, Hutchings M T and Lechner R E 1980 *Phys. Lett.* **80A** 337
- Dickens M H, Hutchings M T, Kjems J and Lechner R E 1978 *J. Phys. C: Solid State Phys.* **11** L583
- Dixon M and Gillan M J 1980 *J. Phys. C: Solid State Phys.* **13** 1919
- Einstein A 1905 *Ann. Phys., Lpz.* **17** 549
- Gillan M J and Dixon M 1980a *J. Phys. C: Solid State Phys.* **13** 1901
- 1980b *J. Phys. C: Solid State Phys.* **13** L835
- Hayes W 1974 (ed.) *Crystals with the Fluorite Structure* (Oxford: Clarendon)
- Hutchings M T, Clausen K, Dickens M H, Hayes W, Kjems J K, Schnabel P G and Smith C 1984 *J. Phys. C: Solid State Phys.* **17** 3903
- Mościński J and Jacobs P W M 1985 *Proc. R. Soc. A* **398** 173
- Rahman A 1976 *J. Chem. Phys.* **65** 4845
- Sangster M J L and Dixon M 1976 *Adv. Phys.* **25** 247