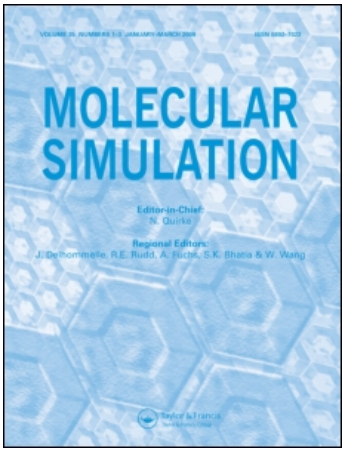

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THE COMPUTER SIMULATION OF URANIUM DIOXIDE†

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We describe how molecular dynamics simulation has been used to study the properties of the nuclear fuel UO_2 and other materials having the same (fluorite) crystal structure. These materials become highly disordered and the anions become very mobile in the high temperature solid. Molecular dynamics has allowed us to investigate the nature of the disorder and to analyze the diffusion process in terms of vacancy and interstitial defects. The simulations have successfully reproduced the ion disordering observed experimentally in UO_2. We discuss the prospects for extending the simulations to include the effects of electronic excitations and electronic polarizability which are known to be important in UO_2.

KEY WORDS: Molecular Dynamics, nuclear fuel, fluorite structure, Uranium Dioxide

Uranium dioxide is the main constituent of the fuel in nuclear reactors, and a thorough understanding of its thermodynamic, mechanical and transport properties is of great importance for the nuclear industry. Because of this, the material has been intensively studied both experimentally and theoretically [1]. In spite of all this work, our fundamental (i.e. microscopic) understanding of its behaviour, especially at high temperatures, remains unsatisfactory. The high temperature region (above say 2500 K) is particularly important, because of its relevance for reactor-safety studies; it is also the region where experiments are most difficult. We believe that atomistic molecular dynamics simulation [2] has much to offer, in complementing and helping to interpret experimental measurements, in building up a realistic picture of the material on the atomic scale, and in giving reliable predictions where experimental information is lacking. We describe in this paper some of the successes that have already been achieved in the simulation of UO_2 and related compounds, and also some of the difficulties that remain to be overcome.

Uranium dioxide is one of a large family of compounds MX_2 having the fluorite structure (figure 1) [3]. In general, materials with this structure are fast ion conductors at high temperatures: above typically 4/5 of the melting point, the anion sublattice becomes heavily disordered, and the mobility of the anions becomes comparable with that found in molten salts [4]. The transition to the fast ion state is usually marked by a pronounced peak in the specific heat, the enthalpy of the transition being comparable to the heat of fusion [5]. The transition occurs smoothly over a range of about 100 K, and is not a phase transition in the thermodynamic sense; in particular, the crystal symmetry stays unaltered through the transition. It has been known for many years that the thermodynamic properties of UO_2 are anomalous at high temperature. Between about 1500 K and the melting point (3120 K) the specific heat rises

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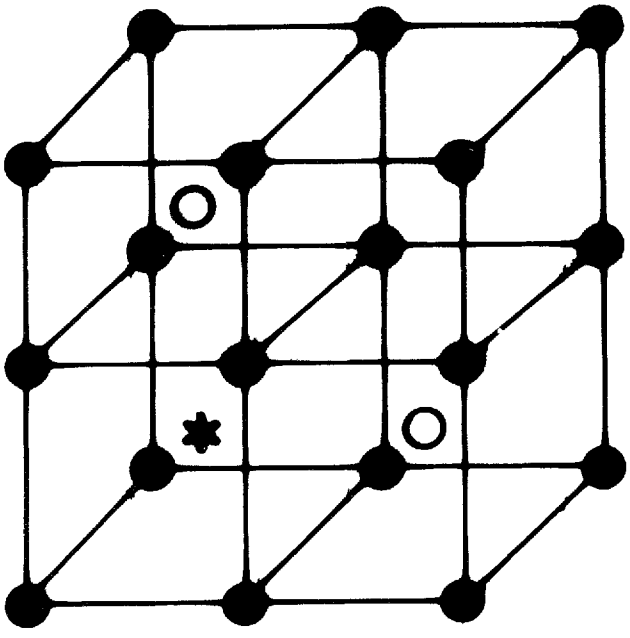

Figure 1 The fluorite lattice: O cation, ● anion, * interstitial site.

from about 9 times the gas constant (i.e. the expected Dulong-Petit value) to roughly twice this value [6]. In this, it appears to differ from the other fluorites, which show a well-defined peak, although there are indications of a small peak at around 2670 K [7]. The reasons for this difference of behaviour are not yet understood. In fact, the existence of fast ion conduction in UO_2 was conjectural until quite recently. However, the presence of a large degree of ionic disorder at high temperatures has now been clearly demonstrated by neutron-scattering measurements [8]. The diffuse transition to the fast-ion state appears to occur at about 2300 K, i.e. about 3/4 of the melting point.

Uranium dioxide differs from most other fluorites in being a semiconductor. The electronic configuration of the uranium ions is U^{4+} ($5f^2$), so that naively one might expect the material to be a metal, since the 5f band is only partially occupied. But because of the narrowness of this band, electron correlations make it a Mott insulator [9]. The lowest-energy excitation process is expected to consist of the transfer of electrons between ions, which can be represented by the disproportionation reaction:

$$2U^{4+} \rightleftharpoons U^{3+} + U^{5+}. \tag{1}$$

Electrical conductivity measurements show that the thermal band gap for these excitations is about 2 eV [10]. This is small enough to give a high degree of electronic disorder as one approaches the melting point. From the data of [11], we estimate that the concentration of electrons (U^{3+}) and holes (U^{5+}) at the melting point will be about 5%. Estimates of Hyland and Ralph [11] indicate that the direct contribution of electronic excitations to the specific heat will be a minor one, but it seems quite possible that the presence of electronic disorder might have a strong influence on the

ionic disorder (and vice versa). This is one possible reason why the high temperature behaviour of UO_2 differs from that of other fluorites.

Clearly UO_2 is a hard problem. Because it is hard, our early simulation work [12–15] in this area at Harwell focussed on the study of fast ion conduction in other fluorites such as CaF_2 and PbF_2, for which there is a wealth of experimental data. This work has been in progress for several years and has given a clear picture of fast ion conduction in these fluorites. In the following section, we shall summarize the achievements of this work. We have begun simulations on UO_2 itself only recently [16]. At this stage, we ignore the electronic excitations, and use the simplest credible interaction model, namely a fully ionic rigid-ion Born-Mayer potential. Given its simplicity, this model is surprisingly successful: our molecular-dynamics calculations correctly reproduce the fast-ion conduction, with a transition temperature which is in quite close agreement with experiment. The thermodynamic functions also well reproduced, except near the melting point. We shall describe some of the main results of this work in section 3. We shall see that in spite of the successes, there are serious problems to be overcome; we shall comment on these in the final section.

2. SIMULATIONS OF FLUORITE MATERIALS

The simulation work has been based on standard molecular dynamics techniques [2], using simple but realistic models for the interionic forces. The task is simplified by the

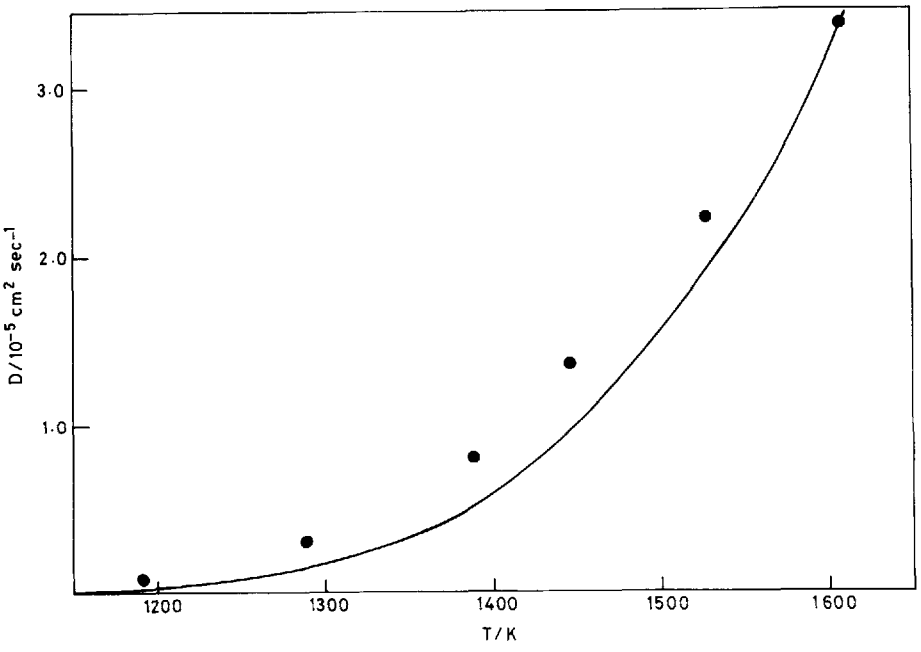

Figure 2 The anion diffusion coefficient from MD simulations of CaF_2 [13] compared with values deduced via the Nernst-Einstein relation from conductivity measurements [18]. Dots show simulation data; curve shows experimental values.

fact that most of the fluorite materials are close to being fully ionic, so that the Coulombic interaction is that of point charges having the full ionic values. The interionic potentials we have used have the Born-Mayer-Huggins form:

$$V_{\alpha\beta}(r) = z_\alpha z_\beta e^2/r + A_{\alpha\beta}\exp(-r/\varrho_{\alpha\beta}) - C_{\alpha\beta}/r^6, \quad (2)$$

where α, β denote the ionic species, z_α are the ionic charges in units of the protonic charge e; the second and third terms on the right represent respectively the short-range repulsion due to electronic overlap and the van der Waals dispersion energy. We have constructed models of this type for the materials CaF_2 [12, 13], $SrCl_2$ [14] and PbF_2 [15], the parameters $A_{\alpha\beta}$, $\varrho_{\alpha\beta}$ and $C_{\alpha\beta}$ being determined partly by fitting to low-temperature data on the perfect crystal, and partly by appeal to previous electronic-structure calculations. It will be noted that the interaction models we use do not explicitly include the effects of electronic polarization. This means, for example, that they give a high frequency dielectric constant ε_∞ equal to unity, whereas the experimental value of ε_∞ is about 2 [3]. This inevitably entails marked discrepancies between the theoretical and experimental phonon frequencies. However, part of the effect of electronic polarization is implicitly accounted for in the empirical fitting of the potential parameters. The problem appears not to be serious for the materials discussed here. It is more serious for UO_2, and we shall return to this question in section 3.

The simulations employ the usual periodic boundary conditions [2], with a cubic supercell. It turns out that quite small supercells give satisfactory results: many of the exploratory calculations were made with systems of 96 ions (32 cations + 64 anions).

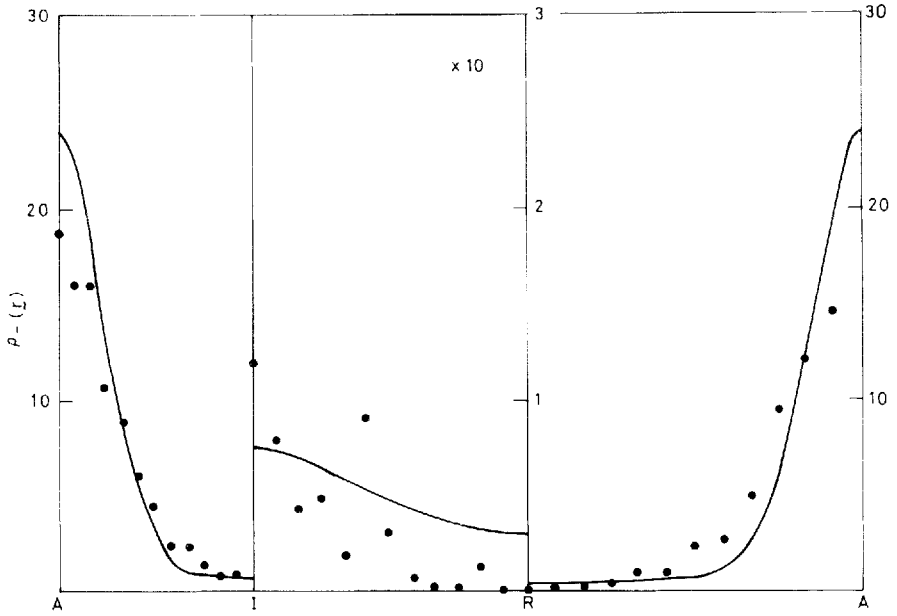

Figure 3 Comparison of anion probability density obtained from simulation of PbF_2 [15] at 991 K and diffraction results [19] at 973 K. Points in the unit cell are: A = regular anion site, I = mid-point of cube edge, R = cube centre. Dots show simulation data; curve shows experimental results. Note the ten-fold magnification of scale in the interval I — R.

With this size of system, the calculations are extremely rapid. For example, a run of 10^4 time steps, which is more than enough to give accurate results for the ionic diffusion coefficient, takes less than 10 minutes on the Cray XMP. However, size effects are not entirely negligible, and it is preferable to work with the next largest system, which contains 324 ions. Very recently, Brass [17] has performed molecular dynamics simulations on fluorites using considerably larger systems. The results confirm that the remaining size effects for systems larger than 324 ions are small.

The simulations have focussed on the analysis of fast ion conduction in the three materials mentioned above. The realism of the simulations can be judged from a comparison of the calculated anion diffusion coefficient D_- as a function of temperature in CaF_2 with the experimental results, which we reproduce in figure 2. The simulations correctly reproduce the rapid increase of D_- around 1400 K to liquid-like values. Diffraction measurements on fluorite materials have allowed an experimental determination of the spatial distribution of the mobile ions in the unit cell in the fast ion state. These measurements also give us a further way of testing the validity of the simulations. In figure 3, we show the simulated and experimental results for the probability distribution of the fluorine ions in PbF_2 above the transition temperature. Although there are quantitative differences, the qualitative features are all well reproduced by the simulations. It will be noted that the probability distribution is concentrated on the regular anion sites, which indicates that the mobile ions spend the majority of their time in vibration about these sites. In both simulation and experiment, the distribution has substantial values around the line passing directly between neighbouring regular sites. This gives an indication of the path followed by the diffusing ions. Finally, one notes that there is only a small probability for finding ions at the cube centre position marked by an asterisk in figure 1. We touch here on a question that has been controversial in the past. The cube centre position is known to be the site occupied by anion interstitials below the transition temperature [20], and it has often been assumed that this site must be substantially occupied in the fast ion state (see e.g. [21]). Both the simulations and the diffraction experiments show that this is not the case.

Further analysis of the simulations has given a more detailed picture of the diffusion mechanism. In all three materials that we have studied, we find that diffusion occurs by discrete, well-defined jumps between the regular anion sites [14, 15, 22]. Most of the jumps ($\sim$ 80%) occur along the $\langle 100 \rangle$ direction between nearest-neighbour sites. Almost all of the remaining jumps are in the $\langle 110 \rangle$ directions between second neighbours, some 1% being of a more complicated type. These conclusions were confirmed by later experiments performed by incoherent quasielastic neutron scattering [23].

The molecular dynamics simulations have been especially helpful in giving an interpretation of the observed phenomena. Two matters have been particularly controversial. One concerns the description of fast ion conduction in terms of lattice defects. At temperatures below the transition, it has been well established for many years that ionic diffusion is due to anion vacancies and interstitials. Given the large values of the diffusion coefficient and the high degree of disorder above the transition, it has not been clear whether a description in terms of isolated vacancies and interstitials remains valid. There have also been strong disagreements about the concentration of such defects in the fast ion state. The second controversial matter concerns the interpretation of measurements using coherent quasielastic neutron scattering [24]. These measurements probe the spectrum of density fluctuations at different wavevec-

tors. The measurements reveal a prominent quasielastic (i.e. zero frequency) peak which is absent below the transition, and whose intensity varies rapidly with wavevector. This indicates the presence of strong decaying density fluctuations with a decay time of order 1 psec, on a length scale related to the wavevector dependence.

We have been able to use the simulations both to clarify the question about defects and to interpret the quasielastic scattering, and to show that the two are intimately related [13, 25]. The fact that diffusion occurs by discrete ionic jumps between regular sites leads to a natural analysis of diffusion in terms of vacancies and interstitials [14, 25]. But there is a crucial difference from the low temperature situation, in that the analysis requires the interstitials to reside on the regular sites. More correctly, we should say that an 'interstitial' consists of a pair of ions which in some sense share the same regular site. The connection between this picture and the quasielastic measurements is made in two steps. Firstly, we analyze the simulations to calculate the density fluctuation spectrum. This has been done for CaF_2, where we have shown that the observed quasielastic peak is quantitatively reproduced in the simulations [13]. By way of illustration, we show in figure 4 a comparison of the wavevector-dependent quasielastic intensity obtained from simulation and experiment respectively. The second step in the connection consists of examining the correlation between the density fluctuations responsible for the quasielastic scattering and the motion of the defects. It turns out that there is an almost perfect correlation [25]. This means that the density fluctuations can be regarded as arising from the disturbance caused by the defects as they jump from site to site. An important part of this conclusion is that the intensity of the observed peak, and its rapid dependence on wavevector come largely from the strong lattice distortion surrounding the defects. Our description here has necessarily been brief; for details the reader should consult the original papers [13, 25, 26].

The overall conclusion from this simulation work on fluorite analogues of UO_2 is

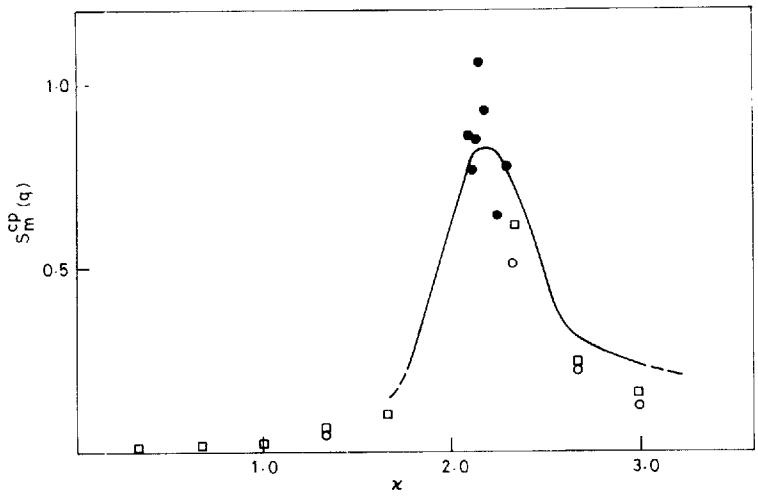

Figure 4 The simulated quasielastic intensity in CaF_2 [13] at 1447 and 1529 K (open circle and square) as a function of wavevector in the ⟨100⟩ direction, compared with experimental results (full circle and curve) at 1473 K [24].

that simple (but carefully constructed) interaction models faithfully reproduce the observed fast ion conduction and can give important new insights into the microscopic processes underlying the phenomena.

3. URANIUM DIOXIDE

We expect UO_2 to be considerably more difficult to model successfully than the materials we have just described, both because of the high polarizability of the ions and because of the electronic excitations alluded to in the Introduction. As an illustration of the polarizability effects, we note that the high frequency dielectric constant ε_∞ in UO_2 is 5.3 [27], whereas a rigid-ion model will necessarily give $\varepsilon_\infty = 1$. Nevertheless, the exploratory simulations begun recently at Harwell [16] are based on rigid-ion potentials having the form given in equation (2), and completely neglect electronic excitation. Full details are given in a recent publication [16]. The results obtained so far are surprisingly good, as we now describe.

The simulations performed to date employ a small repeating cell of 96 ions, which previous work has shown to be adequate for semi-quantitative purposes. In most of the work, we have used the recently developed constant-pressure constant-temperature molecular dynamics technique [28]. This allows us to pre-set the required pressure (usually zero) and temperature. A series of simulations has been performed

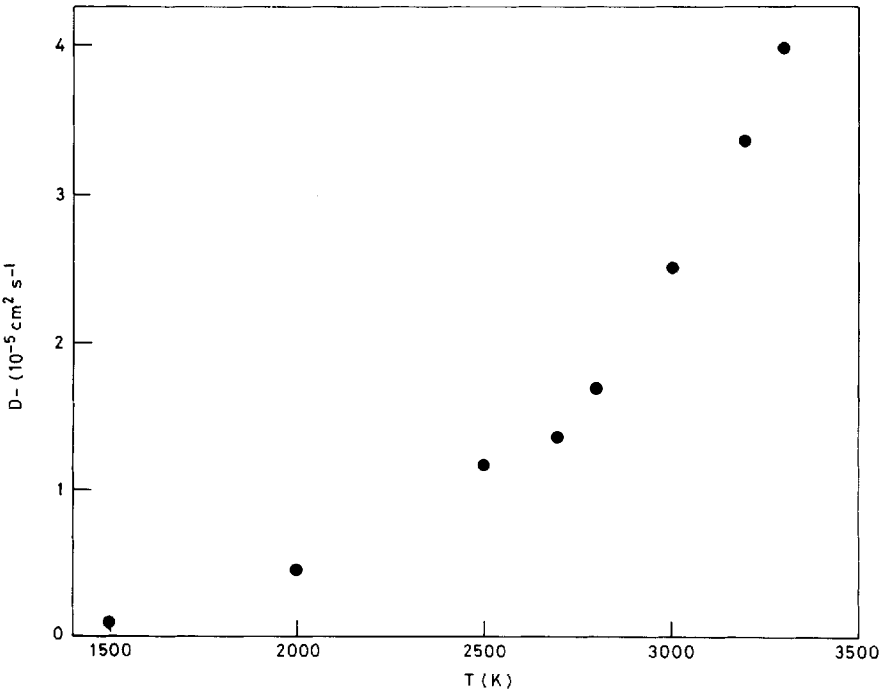

Figure 5 Simulation results [16] for the oxygen diffusion coefficient D_- in solid UO_2 as a function of temperature.

for a range of temperatures in both the solid and the liquid. Our results for the oxygen diffusion coefficient in the solid (figure 5) show the onset of fast ion conduction at about 2300 K. This is in close accord with the recent neutron diffraction measurements [8]. These measurements in fact probe ionic disorder rather than the diffusion itself, but we expect the two to be closely linked. The experiments show that disorder on the oxygen sublattice begins to become substantial at around 2300 K.

We have also used the simulations to calculate the volume and the enthalpy as a function of temperature. The comparisons with experiment are shown in figures 6 and 7. The agreement is quite satisfactory up to about 2300 K, but is not good above this. In particular, we are missing the substantial increase in specific heat at high temperatures revealed by experiment. Values for the specific heat deduced from our results in the region of 3000 K lie only a little above the Dulong-Petit value, instead of being about twice this value as required by experiment. We have suggested [16] that this may be because the observed increase of specific heat is due to electronic

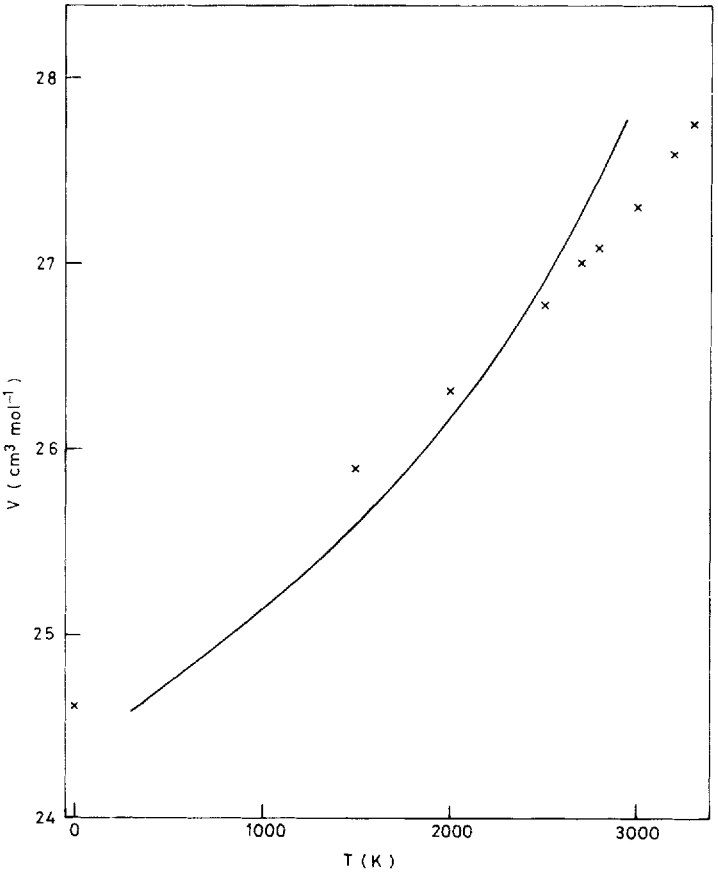

Figure 6 Comparison of simulated and experimental values of the molar volume of solid UO_2 as a function of temperature. Crosses show results from simulation [16], curve shows values deduced from neutron diffraction measurements of the lattice parameter [29].

excitations. However, this would be in conflict with the conclusions drawn by other workers [11], and we admit that at present we are not sure.

Our simulated system melts spontaneously at between 3300 K and 3400 K, which is very close to the experimental melting point of 3120 K. Melting is readily detectable in the simulations by the sharp increase in the cation diffusion coefficient. Unfortunately, the simulated properties of the liquid are not in good agreement with experimental data. Firstly, the volume increase on melting is much too great. We find an increase of 39%, which is to be compared with the experimental value of 10%. Secondly, our expansion coefficient for the liquid is much too low (by about a factor of 5).

The conclusion we draw from this preliminary work is that the interaction model we are presently using is highly successful in some respects but rather poor in others. We reproduce the onset of fast ion conduction, the thermodynamic properties of the

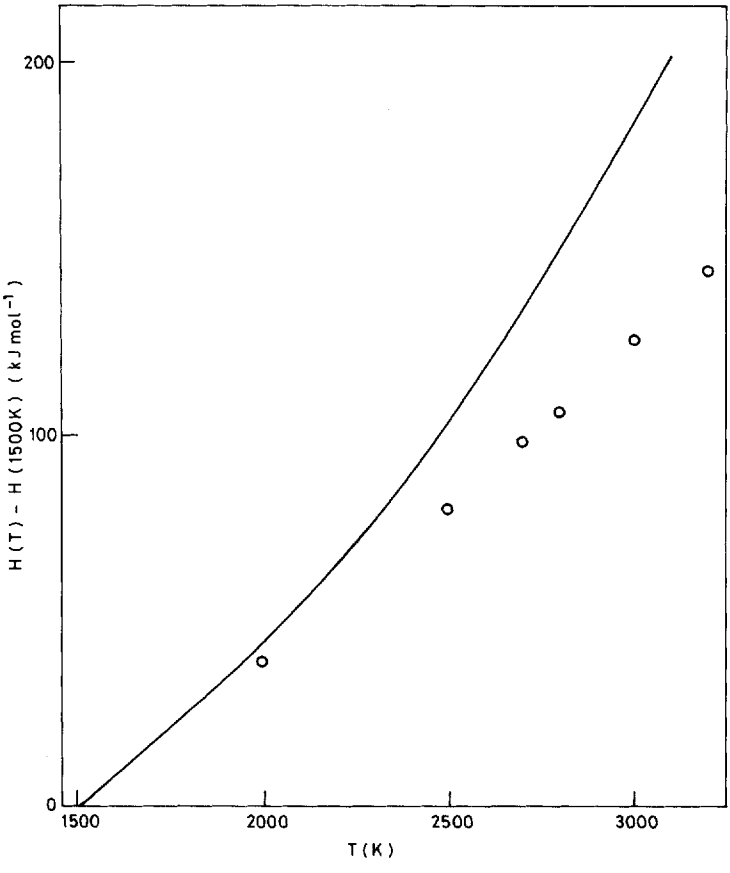

Figure 7 Comparison of simulated and experimental values of the enthalpy of solid UO_2 relative to its value at 1500 K. Solid curve shows measured values from the compilation of Fink et al. [30]; circles show simulation results.

solid and the melting point fairly satisfactorily, but our problems with the liquid indicate that the interaction model cannot be full realistic.

4. FUTURE PROSPECTS

We have shown how molecular dynamics simulation, taken in conjunction with experiments, has helped to deepen our understanding of fast ion conduction in fluorite materials. The simulation results for UO_2 itself represent only a start, but they are promising. We have pointed out that the temperature dependence of the specific heat of UO_2 differs markedly from that of the other fluorites, and we have speculated that the difference may be caused by electronic excitations. We plan to extend the simulations in order to study the effect of electronic excitations on the fast ion conduction. The inclusion of electronic excitations in a molecular dynamics simulation would normally be impossible, because of the importance of quantum effects. It is possible here because of the special feature that the effect of the excitations is mainly to alter the charge on the ions (equation (1)). What will be needed, then, is simulations in which some of the U^{4+} are converted to U^{3+} and U^{5+}. To represent thermal equilibrium, we shall also need to allow transfer of the 'electrons' and 'holes' between the ions. We expect that our present simulation model, although far from perfect, will form an adequate basis for this generalization.

Clearly it will also be important to improve the interaction model for UO_2. The most obvious deficiency in the present model is its neglect of polarization effects. The usual method of including such effects is via the shell model [31], in which each ion is represented by a core and a shell, both carrying a charge, the two being coupled by a harmonic spring. Molecular dynamics simulation using the shell model is feasible [32], though it is not often used, because the techniques currently available are rather demanding on computer time. However, we believe that there is considerable scope for improving these techniques and we feel confident that shell-model simulation of UO_2 will prove practicable.

Acknowledgement

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