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## COMMENT

# A comment on a rigid-ion potential for $\text{UO}_2$

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**Abstract.** We report a revision of the rigid-ion potential for  $\text{UO}_2$  introduced by Sindzingre and Gillan. In its original form, the potential is unstable at the reported lattice parameter. We have re-fitted the potential to remove this problem, whilst keeping as close as possible to the original parametrization. The calculated static quantities are little changed, but there is a small increase in the O Frenkel pair formation energy. In dynamics both the superionic transition temperature and the rate of O diffusion in the superionic state are altered, but there is no effect on the calculated thermal conductivity. The conclusions of previous work with the original potential are not affected by the changes we propose.

## 1. Introduction

Current interest in the modelling and simulation of  $\text{UO}_2$  (Sindzingre and Gillan 1988, Gillan 1989, Lindan and Gillan 1991, 1994, Lindan 1994) is encouraging the re-examination and improvement of existing potentials. In the course of developing a charge-transfer model based on the rigid-ion potential of Sindzingre and Gillan, we have encountered a problem with the latter. Specifically, the model is unstable at the reported lattice parameter of 5.4680 Å. This is evident from the phonon spectrum for the model, which we have calculated using our own lattice dynamics code, where the (100) Raman mode becomes imaginary near the zone boundary. We have confirmed this using the Harwell CASCADE program (Catlow and Mackrodt 1982, Norgett 1974) to calculate the phonons (after addressing some technical points, which we discuss in section 2). The softening of the Raman mode suggests that the O ions will not occupy their regular lattice sites in the lowest-energy configuration, a fact we have verified through relaxation of the structure at constant volume. It should be recalled that this rigid-ion model was developed from a shell model (Jackson *et al* 1986), which does not display any such instability. Additionally we have found that the same problem exists with an earlier  $\text{UO}_2$  rigid-ion model (Walker and Catlow 1981), which was also developed from another (stable) shell model using essentially the same procedure. It is therefore natural to examine this procedure and to revise the fitting to remove the problem.

## 2. Modification of the potential

The rigid-ion potential of Sindzingre and Gillan takes the form

$$V_{\alpha,\beta} = \frac{z_\alpha z_\beta e^2}{4\pi\epsilon_0 r} + A_{\alpha,\beta} \exp(-r/\rho_{\alpha,\beta}) - \frac{C_{\alpha,\beta}}{r^6} \quad (1)$$

where  $z_\alpha$  is the charge on species  $\alpha$ ,  $e$  is the protonic charge,  $\epsilon_0$  is the permittivity of free space and  $r$  the interionic separation. The charges are +4 and -2 for U and O respectively.

The short-range parameters are shown in table 1(a). Sindzingre and Gillan made two modifications to the shell model of Jackson *et al* to obtain these parameters. Firstly, they discarded the shell-core springs, leaving rigid ions with formal charges. Then, in order to yield an O Frenkel pair formation energy  $E_F$  close to that of the shell model (4.76 eV), they adjusted the values of  $A_{+-}$  and  $\rho_{+-}$ , keeping the lattice constant fixed. We have found that it is this latter modification that introduces the imaginary phonons, and accordingly we have re-fitted the model by adjustment of the same two parameters, with the additional demand that the Raman mode frequencies remain real throughout the Brillouin zone.

**Table 1.** (a) Potential parameters for the rigid-ion model of  $\text{UO}_2$ , taken from Sindzingre and Gillan (1988). Energies are in electron volts, distances in Å. The anion-anion potential and its first and second derivatives are continuous across the spline points. (b) The modified cation-anion interaction for the re-fitted potential. All other parameters are unchanged.

(a)	
$V_{++}^{\text{sr}}$	= 0
$V_{+-}^{\text{sr}}$	= $869.98 \exp(-r/0.4270) - 65.4/r^6$
$V_{--}^{\text{sr}}$	= $11\,272.6 \exp(-r/0.1363)$ <span style="float: right;"><math>r &lt; 1.2</math></span>
	= fifth-degree polynomial <span style="float: right;"><math>1.2 &lt; r &lt; 2.1</math></span>
	= third-degree polynomial <span style="float: right;"><math>2.1 &lt; r &lt; 2.6</math></span>
	= $-134.0/r^6$
(b)	
$V_{+-}^{\text{sr}}$	= $895.5898 \exp(-r/0.42512) - 65.4/r^6$

**Table 2.** Calculated and experimental quantities for  $\text{UO}_2$ . The quantities are the elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ , the static dielectric constant  $\epsilon_s$ , the lattice energy  $H$  per molecule and the O Frenkel pair formation energy  $E_F$ . The calculations are for the rigid-ion potential of Sindzingre and Gillan (1988), (a) as given in the original reference, and (b) as calculated by us; the present model; and the shell model of Jackson *et al* (1988). Experimental values are those quoted by Jackson *et al*, except the defect energy which is taken from Matzke (1987). In all cases the lattice parameter is 5.4680 Å.

	Sindzingre and Gillan (1988)		Present model	Shell model	Experiment
	(a)	(b)			
$c_{11}$ (GPa)	380	371	370	400.6	389.3
$c_{12}$ (GPa)	97	86.1	87.6	129.4	118.7
$c_{44}$ (GPa)	79	60.4	69.8	72.2	59.7
$\epsilon_s$	21.4	20.2	18.5	21	24
$H$ (eV)	—	100.72	100.60	—	106.7
$E_F$ (eV)	4.8	4.99	5.20	4.76	3.5–4.5

Before discussing our results, mention must be made of the cut-off radii used in CASCADE for the evaluation of the short-range energy, and for the Ewald summation. It appears (from our efforts to reproduce the calculations of Sindzingre and Gillan) that the original rigid-ion potential was parametrized using a short-range cut-off  $r_c$  equal to the lattice parameter  $a_0$ , 5.4680 Å. As pointed out by Sindzingre and Gillan, the contributions of the Van der Waals terms in the potential are not negligible at this separation. To achieve convergence of such quantities as the elastic constants and defect energies we have found it necessary to set  $r_c$  to 1.5 times the lattice parameter. Thus, as will be shown, our calculated static quantities for the original model differ noticeably from those reported by Sindzingre and

Gillan. A second technical point concerns the Ewald summation, for which the real- and reciprocal-space cut-offs are determined in CASCADE through a single accuracy parameter ACCM. If the recommended value (Leslie and Smith 1989) of  $\text{ACCM} = 10^6$  is used for this potential (along with  $r_c = a_0$ ), no imaginary phonon frequencies result. Increasing the value of ACCM to  $10^{11}$  or greater reveals the imaginary frequencies. This indicates that some care is needed in setting the parameters for CASCADE. We note that once sufficient accuracy in the Ewald summation is used, the potential is unstable with any value of  $r_c$ .

### 3. Results

Using  $r_c = 1.5a_0$  and  $\text{ACCM} = 10^{16}$  in CASCADE, we have re-fitted the potential. Our new potential parameters are shown in table 1(b). With these parameters the minimum in energy occurs at a lattice parameter of 5.4680 Å, and at this value there are no imaginary phonon frequencies at the Brillouin zone boundary. The calculated static quantities for our model are shown in table 2, where we compare them with the same quantities calculated for the original potential. In both cases,  $r_c$  and ACCM are the same, with only  $A_{+-}$  and  $\rho_{+-}$  being different for the two calculations. We also show the experimental values, and the calculated values of Sindzingre and Gillan.

**Table 3.** Comparison of the calculated O self-diffusion coefficient  $D_-$  and the thermal conductivity  $\lambda$  for the original potential (Sindzingre and Gillan 1988) and our revised version (present model). Values of the thermal conductivity for the original model are taken from Lindan and Gillan (1991); two comparisons of  $\lambda$  are made at the temperatures shown in parenthesis.

	Sindzingre and Gillan		Present model	
	96 ions	324 ions	96 ions	324 ions
$D_-$ ( $10^{-5}\text{cm}^2 \text{s}^{-1}$ )	2.87	2.36	2.18	1.52
$\lambda$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	2.3 (2000 K)	—	2.3 (1987 K)	—
	1.5 (3007 K)	—	1.3 (3088 K)	—

Overall there is little change in the static dielectric constant or the elastic constants, although  $c_{44}$  is considerably bigger. There is an increase in the value of  $E_F$ , which is about 10% larger than the 4.76 eV found for the shell model (Jackson *et al* 1986). We note that most of the increase occurs when the Raman zone-boundary frequency becomes real, a point we will return to shortly.

It is worth remarking that the problems in constructing a rigid-ion model for  $\text{UO}_2$ , which has a large high-frequency dielectric constant  $\epsilon_\infty$  of 5.3, demonstrate that ionic polarizability is an important feature of the material. Similar problems have arisen in fitting a rigid-ion model for  $\text{PbF}_2$  (Gillan, private communication), which has  $\epsilon_\infty = 3.08$  (Samara 1976), while for  $\text{CaF}_2$ , with  $\epsilon_\infty = 2.06$  no difficulty is found (Dixon and Gillan 1980). Thus for fluorite materials with highly polarizable ions, it may not be possible to develop a rigid-ion description from a shell model such that the two yield the same  $E_F$ , without making more serious compromises in the parametrization and predicted properties.

We have performed molecular dynamics simulations, using both the old and the new potential parameters, in order to ascertain the effect of the change in the potential on the dynamical properties. In these simulations, Coulomb interactions were evaluated using the Ewald summation, with inverse length parameter  $\alpha = 5.6/L$ ,  $L$  being the length of the (cubic) simulation box. Real-space interactions were cut at  $0.5L$ , while in reciprocal space

we evaluated wavevectors within a sphere of  $5(2\pi/L)$  for 96 ions, and  $6(2\pi/L)$  for 324 ions. The molar volume was set equal to the experimental value (MacDonald 1985) at the appropriate temperature, and a time step of 3 fs was used in all the simulations.

We examined the O diffusion coefficient  $D_{-}$  in the superionic state at 3000 K, calculated from the long-time slope of the mean squared displacement of the ions. We used Nosé *NVT* molecular dynamics for 96- and 324-ion systems, the pseudomasses being  $10^{-44}$  and  $10^{-43}$  J s<sup>2</sup> respectively. The simulation time was 81 ps for each system, after 30 ps of equilibration. As a second test, we calculated the thermal conductivity  $\lambda$  using the Green-Kubo method described by Lindan and Gillan (1991), for a microcanonical system of 96 ions at 1987 K and 3088 K (with the Ewald parameter and cut-offs as before). The simulation time, after 150 ps of equilibration, was 1500 ps and 600 ps for the lower and higher temperatures respectively.

The results of these simulations are shown in table 3. In both systems the O diffusion coefficient is rather lower for the new potential parameters, especially for the bigger system. This is not surprising since it is expected that both the superionic transition temperature and the rate of diffusion at a given temperature are sensitive to the value of  $E_F$  (Walker *et al* 1982). It is also clear that the softening of the Raman mode plays a role in these results: it will be recalled that for  $r_c = a_0$  (corresponding in this context to a 96-ion system), Sindzingre and Gillan's model gives imaginary zone-boundary frequencies. In fact, this is true for the new parametrization as well, which, coupled to the lowering of  $E_F$  on the appearance of the soft mode we mentioned earlier, explains the better agreement for the 96-ion simulations, since the defect energies are more nearly equal. (This is true notwithstanding the fact that the Raman mode becomes soft as the lattice parameter is increased, because the defect energies will be more nearly equal, in the 96-ion system, for *any* lattice parameter.) Previous studies (Sindzingre and Gillan 1988, Gillan 1989) of  $\text{UO}_2$  superionic conduction and thermodynamics using the original potential have exclusively employed 96-ion systems, and we believe that the findings of these studies remain valid. Interestingly, the 324-ion diffusion coefficients calculated with the modified potential agree rather well with those obtained using shell-model molecular dynamics (Lindan and Gillan 1994).

There is no significant difference between the values of the thermal conductivity calculated with the old and new potential parameters. Since heat is transported in the crystal by all the normal modes, and our modifications to the potential leave the phonon spectrum mostly unchanged, it is reasonable to find that the modifications do not alter the thermal conductivity at low temperatures. The contribution to  $\lambda$  from ionic conduction in the superionic regime will of course be different, because of the change in the superionic transition temperature and the magnitude of the O diffusion. However, the discrepancy in  $\lambda$  at the higher temperature is well within the statistical errors present in the calculations. Therefore, the conclusions drawn from previous calculations (Lindan and Gillan 1991) of the thermal conductivity of  $\text{UO}_2$ , which used the original potential, are unchanged.

#### 4. Conclusions

We have modified the rigid-ion  $\text{UO}_2$  potential of Sindzingre and Gillan, which is unstable at the reported lattice parameter. Our re-fitting removes the instability, and the small differences in parametrization result in modest changes in the calculated static quantities. The dynamical behaviour is affected, notably by a reduction of the calculated O diffusion coefficient in the superionic state, though the thermal conductivity is not altered. These changes do not affect the conclusions of previous studies made with the original potential

(Sindzingre and Gillan 1988, Gillan 1989, Lindan and Gillan 1991). The problems we have encountered emphasize the importance of ionic polarizability in modelling  $\text{UO}_2$ .

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