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## Derivation of potentials for the rare-earth fluorides, and the calculation of lattice and intrinsic defect properties

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**Abstract.** A detailed reappraisal of the computer modelling of the rare-earth fluorides is presented. A new set of interionic potentials is obtained by empirical fitting to crystal structural data alone. These potentials are then tested by calculation of elastic and dielectric constants, whose values agree favourably with those measured experimentally. Calculations are then presented of the basic defect formation energies for each material, and predictions of the expected type of intrinsic disorder made.

### 1. Introduction

The rare-earth fluoride series, from LaF<sub>3</sub> to LuF<sub>3</sub>, has recently attracted renewed interest, since the lanthanides, when used to dope materials such as CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> and BaLiF<sub>3</sub>, give rise to important applications as optical devices (e.g. solid state lasers and scintillators). In addition, the rare-earth fluorides themselves have potential applications as fast-ion conductors. Recently computational techniques have been used to study the doping of BaLiF<sub>3</sub> with divalent ions [1, 2] and with trivalent ions (Y, La and Nd) [3], partly making use of interionic potentials published by Corish *et al* [4]. The motivation for the present study came when the study of doping was extended to the whole lanthanide series, and it was found that some of the earlier published potentials did not reproduce the crystal structures of the rare-earth fluorides themselves. It is noted that this is not particularly surprising, since the potentials were not obtained empirically, but were calculated explicitly to study effects of doping, using electron-gas methods.

The present paper presents a new set of interatomic potentials for the rare-earth fluorides, which have been obtained by empirical fitting to structures alone. They are validated by calculation of elastic and dielectric constants, which agree with available experimental values. In addition, the intrinsic defect behaviour of the rare-earth fluorides is studied by calculation of basic defect energies for each material.

In section 2, the empirical fitting procedure, and the type of potential employed, are described, followed by a discussion of the calculation of defect properties; section 3 summarizes the available structural data for the rare-earth fluorides, and section 4 discusses the results of the fitting procedure. Finally, in section 5 the results of defect calculations are discussed.

## 2. Computational techniques

### 2.1. Empirical potentials and calculation of lattice properties

The computational method used in this paper is based on empirical potential fitting [5] and lattice energy minimization, employing the General Utility Lattice Program (GULP) [6], in which materials are described in terms of ions interacting through effective potentials. Having derived these potentials, the lattice energy of the material is minimized by varying the structural parameters (atomic positions and lattice parameters). Values of lattice properties, such as elastic and dielectric constants, are calculated for the minimum energy structure. A similar procedure, adopted for the BaLiF<sub>3</sub> structure, is described in [1].

The potential model employed for the rare-earth fluorides is as follows:

- (i) the rare-earth ion RE<sup>3+</sup> is described as rigid, as ionic polarizability is expected to be negligible;
- (ii) a shell model is employed for the F<sup>-</sup> ion;
- (iii) a Born–Mayer potential supplemented by an electrostatic term is specified between the RE<sup>3+</sup> ion and the F<sup>-</sup> shell, having the following form:

$$V(r_{ij}) = q_i q_j / r_{ij} + A \exp(-\rho / r_{ij})$$

where  $q_i$  and  $q_j$  are the ion charges, and  $A$  and  $\rho$  are empirically fitted potential parameters;

- (iv) a four-range Buckingham potential is used to describe the F<sup>-</sup>–F<sup>-</sup> interaction as used in [4].

The empirical fitting procedure, as applied to the RE<sup>3+</sup>–F<sup>-</sup> interactions, was carried out as follows. The appropriate RE<sub>3</sub> structure is input, along with starting values of  $A$  and  $\rho$  parameters from previous calculations (values from [4] were used where available). An initial calculation was carried out to fit the  $A$  parameter alone, and then the new  $A$  parameter was input, and the  $\rho$  parameter fitted. This procedure was used to generate the potentials reported in table 2.

### 2.2. Calculation of defect properties

Defects are modelled using the Mott–Littleton approximation [7, 8] in which a spherical region of lattice surrounding the defect is treated explicitly, with all interactions being considered (region I), and more distant parts of the lattice are treated as a dielectric continuum (region IIB). An interface region (IIA) ensures smooth convergence between explicitly summed and continuum regions. It is important to ensure that region I is large enough to ensure convergence of energy, and in these calculations, radii of 10 and 15 Å respectively were used for regions I and IIA, leading to 530–650 ions in region I and 1300–1500 ions in region IIA.

## 3. Survey of experimental structural data

Experimental structural data on the rare-earth fluorides have come from a number of sources. In most cases the data were obtained from the Inorganic Crystal Structure Database held at Daresbury Laboratory [9]. Table 1 gives the individual references. In a few cases structural data were obtained from the compilation by Wyckoff [10]. The structures are all described by one of two possible space groups. From La to Nd, the space group is  $P\bar{3}c1$  (number 165), hexagonal, and from Sm to Lu, it is  $Pnma$  (number 62), orthorhombic. Note that no structure could be found for PmF<sub>3</sub>.

**Table 1.** Structural references for the rare-earth fluorides.

System	Ref.
LaF <sub>3</sub>	[11]
CeF <sub>3</sub>	[12]
PrF <sub>3</sub>	[13]
NdF <sub>3</sub>	[14]
SmF <sub>3</sub>	[15]
EuF <sub>3</sub>	[10]
GdF <sub>3</sub>	[10]
TbF <sub>3</sub>	[16]
DyF <sub>3</sub>	[10]
HoF <sub>3</sub>	[16]
ErF <sub>3</sub>	[17]
TmF <sub>3</sub>	[10]
YbF <sub>3</sub>	[15]
LuF <sub>3</sub>	[10]

**Table 2.** Potential parameters used in the calculations.

Interactions	Potential type	<i>A</i> (eV)	$\rho$ (Å)	<i>C</i> (eV Å <sup>6</sup> )	
La <sub>core</sub> -F <sub>shell</sub>	Buckingham	2817.74	0.2980	0.0	
Ce <sub>core</sub> -F <sub>shell</sub>	Buckingham	2627.13	0.2980	0.0	
Pr <sub>core</sub> -F <sub>shell</sub>	Buckingham	2453.39	0.2980	0.0	
Nd <sub>core</sub> -F <sub>shell</sub>	Buckingham	2488.27	0.2950	0.0	
Sm <sub>core</sub> -F <sub>shell</sub>	Buckingham	1764.57	0.3064	0.0	
Eu <sub>core</sub> -F <sub>shell</sub>	Buckingham	2085.74	0.2950	0.0	
Gd <sub>core</sub> -F <sub>shell</sub>	Buckingham	1667.02	0.3037	0.0	
Tb <sub>core</sub> -F <sub>shell</sub>	Buckingham	1541.15	0.3065	0.0	
Dy <sub>core</sub> -F <sub>shell</sub>	Buckingham	1536.68	0.3037	0.0	
Ho <sub>core</sub> -F <sub>shell</sub>	Buckingham	2590.91	0.2809	0.0	
Er <sub>core</sub> -F <sub>shell</sub>	Buckingham	1880.44	0.2920	0.0	
Tm <sub>core</sub> -F <sub>shell</sub>	Buckingham	1390.19	0.3037	0.0	
Yb <sub>core</sub> -F <sub>shell</sub>	Buckingham	2381.55	0.2808	0.0	
Lu <sub>core</sub> -F <sub>shell</sub>	Buckingham	1448.23	0.2990	0.0	
F <sub>shell</sub> -F <sub>shell</sub>	Buckingham (4 regions)	1127.7	0.2753	15.83	$r_1 = 2.0 \text{ Å}$ $r_{min} = 2.79 \text{ Å}$ $r_2 = 3.031 \text{ Å}$
		<i>k</i> (eV Å <sup>-2</sup> )	<i>Y<sub>shell</sub></i> ( e )		
F <sub>core</sub> -F <sub>shell</sub>	Harmonic spring	20.77	-1.59		

#### 4. Results: interatomic potentials and perfect lattice properties

The first aim of this study was to fit new potentials to the structures of the rare-earth fluorides. As noted in section 2.1, a consistent F<sup>-</sup>-F<sup>-</sup> potential was maintained, which was identical to that obtained in [4]. Table 2 lists the potentials, including the F<sup>-</sup>-F<sup>-</sup> potential [4], and table 3 gives the comparison between experimental and calculated lattice parameters. Tables 4 and 5 give a similar comparison for the positions of the ions in each of the two structure types.

**Table 3.** Lattice parameters of the rare-earth fluorides: experimental values in brackets, and calculated values from potentials in [4] in italics.  $\Delta a$ ,  $\Delta b$ ,  $\Delta c$  and  $\Delta V$  refer to the percentage difference between experimental values and those calculated using the potentials obtained in this paper.

<i>P</i> $\bar{3}$ <i>c</i> 1 structures (hexagonal)							
System	<i>a</i> (Å)		<i>c</i> (Å)	$\Delta a$ (%)		$\Delta c$ (%)	$\Delta V$ (%)
LaF <sub>3</sub>	7.183 (7.185) <i>7.101*</i>		7.314 (7.351) <i>7.216*</i>	-0.02		-0.5	-0.55
CeF <sub>3</sub>	7.127 (7.131)		7.247 (7.286)	-0.06		-0.53	-0.65
PrF <sub>3</sub>	7.076 (7.075)		7.185 (7.234)	0.01		-0.68	-0.66
NdF <sub>3</sub>	7.032 (7.030)		7.135 (7.200)	0.03		-0.9	-0.84
<i>Pnma</i> structures (orthorhombic)							
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\Delta a$ (%)	$\Delta b$ (%)	$\Delta c$ (%)	$\Delta V$ (%)
SmF <sub>3</sub>	6.579 (6.676)	7.016 (7.062)	4.436 (4.411)	-1.45	-0.65	0.56	-1.54
EuF <sub>3</sub>	6.396 (6.622) <i>6.845*</i>	6.927 (7.019) <i>7.160*</i>	4.479 (4.396) <i>4.338*</i>	-3.41	-1.32	1.89	-2.88
GdF <sub>3</sub>	6.279 (6.570) <i>6.800*</i>	6.910 (6.984) <i>7.120*</i>	4.554 (4.393) <i>4.364*</i>	-4.43	-1.06	3.67	-1.97
TbF <sub>3</sub>	6.220 (6.513) <i>6.800*</i>	6.904 (6.949) <i>7.127*</i>	4.582 (4.384) <i>4.368*</i>	-4.51	-0.65	4.52	-0.84
DyF <sub>3</sub>	6.079 (6.460)	6.875 (6.906)	4.613 (4.376)	-5.8	-0.45	5.4	-1.24
HoF <sub>3</sub>	6.172 (6.404)	6.828 (6.875)	4.522 (4.379)	-3.63	-0.68	3.27	-1.15
ErF <sub>3</sub>	6.005 (6.341) <i>6.766*</i>	6.832 (6.834) <i>7.104*</i>	4.601 (4.371) <i>4.348*</i>	-5.3	-0.04	5.26	-0.35
TmF <sub>3</sub>	5.818 (6.283)	6.881 (6.811)	4.670 (4.408)	-7.4	1.02	5.95	-0.88
YbF <sub>3</sub>	5.986 (6.218) <i>6.681*</i>	6.795 (6.785) <i>7.043*</i>	4.578 (4.431) <i>4.345*</i>	-3.73	0.15	3.33	-0.38
LuF <sub>3</sub>	5.689 (6.151) <i>6.759*</i>	6.884 (6.758) <i>7.100*</i>	4.681 (4.476) <i>4.360*</i>	-7.51	1.87	4.59	-1.43

**Table 4.** Fractional coordinates of the ions in the  $P\bar{3}c1$  structures, with experimental values in brackets. Note that F3 is at  $(0, 0, \frac{1}{4})$ .

System	RE at	F1 at $(x, y, z)$			F2 at
	$(u, 0, \frac{1}{4})$	$x$	$y$	$z$	$(\frac{1}{3}, \frac{1}{2}, v)$
LaF <sub>3</sub>	0.6593 (0.6609)	0.3633 (0.3667)	0.0516 (0.0540)	0.0809 (0.0824)	0.1748 (0.1855)
CeF <sub>3</sub>	0.6588 (0.6607)	0.3647 (0.3659)	0.0539 (0.0540)	0.0804 (0.0824)	0.1725 (0.1871)
PrF <sub>3</sub>	0.6584 (0.6592)	0.3656 (0.3670)	0.0556 (0.0557)	0.0800 (0.0796)	0.1714 (0.1837)
NdF <sub>3</sub>	0.3417 (0.3414)	0.3096 (0.3104)	0.0564 (0.0579)	0.0797 (0.0805)	0.3288 (0.3145)

**Table 5.** Fractional coordinates of the ions in the  $Pnma$  structures, with experimental values in brackets.

System	RE at $(u, \frac{1}{4}, v)$		F1 at $(x, y, z)$			F2 at $(w, \frac{1}{4}, t)$	
	$u$	$v$	$x$	$y$	$z$	$w$	$t$
SmF <sub>3</sub>	0.3598 (0.3660)	0.0442 (0.0619)	0.1699 (0.1650)	0.0672 (0.0660)	0.3925 (0.3906)	0.5164 (0.5205)	0.6645 (0.6730)
EuF <sub>3</sub>	0.3616 (0.3530)	0.0418 (0.0380)	0.1706 (0.1650)	0.0654 (0.0600)	0.3800 (0.3630)	0.5192 (0.5280)	0.5951 (0.6010)
GdF <sub>3</sub>	0.3621 (0.3530)	0.0361 (0.0380)	0.1703 (0.1650)	0.0645 (0.0600)	0.3683 (0.3630)	0.5224 (0.5280)	0.6046 (0.6010)
TbF <sub>3</sub>	0.3626 (0.3680)	0.0341 (0.0610)	0.1703 (0.1650)	0.0643 (0.0660)	0.3639 (0.3840)	0.5239 (0.5220)	0.6086 (0.5840)
DyF <sub>3</sub>	0.3643 (0.3530)	0.0320 (0.0380)	0.1708 (0.1650)	0.0638 (0.0600)	0.3571 (0.3630)	0.5263 (0.5280)	0.6151 (0.6010)
HoF <sub>3</sub>	0.3639 (0.3670)	0.0382 (0.0590)	0.1719 (0.1660)	0.0641 (0.0660)	0.3686 (0.3770)	0.5223 (0.5250)	0.6050 (0.5840)
ErF <sub>3</sub>	0.3655 (0.3677)	0.0327 (0.0608)	0.1718 (0.1638)	0.0636 (0.0639)	0.3563 (0.3781)	0.5263 (0.5228)	0.6162 (0.5875)
TmF <sub>3</sub>	0.3681 (0.3530)	0.0298 (0.0380)	0.17097 (0.1650)	0.0634 (0.0600)	0.3444 (0.3630)	0.5301 (0.5280)	0.6273 (0.6010)
YbF <sub>3</sub>	0.3659 (0.3672)	0.0341 (0.0538)	0.1726 (0.1646)	0.0635 (0.0633)	0.3581 (0.3675)	0.5254 (0.5269)	0.6353 (0.6510)
LuF <sub>3</sub>	0.3698 (0.3530)	0.0302 (0.0380)	0.1712 (0.1650)	0.0633 (0.0600)	0.3396 (0.3630)	0.5307 (0.5280)	0.6321 (0.6010)

In table 3, it can be seen that agreement for the structures of space group  $P\bar{3}c1$  (LaF<sub>3</sub> to NdF<sub>3</sub>) is better than 1%, whereas for the structures of space group  $Pnma$ , it is around 5% on average. It proved impossible to obtain better agreement than this, which may be due to the greater complexity of the orthorhombic structures. This trend is repeated in tables 4 and 5,

**Table 6.** Calculated elastic constants for the  $P\bar{3}c1$  structures, with experimental values in brackets.

System	Elastic constants ( $10^{10}$ N m $^{-2}$ )					
	$c_{11}$	$c_{12}$	$c_{13}$	$c_{33}$	$c_{44}$	$c_{66}$
LaF $_3$	22.7 (18.0 $\pm$ 0.1)	9.9 (8.8 $\pm$ 0.4)	7.7 (5.9 $\pm$ 0.5)	26.9 (22.2 $\pm$ 0.1)	5.2 (3.4 $\pm$ 0.2)	6.4 (4.6 $\pm$ 0.2)
CeF $_3$	23.6 (18.2 $\pm$ 0.1)	10.5 (8.8 $\pm$ 0.4)	8.5 (6.3 $\pm$ 0.3)	27.2 (22.6 $\pm$ 0.1)	5.7 (3.6 $\pm$ 0.1)	6.6 (4.7 $\pm$ 0.2)
PrF $_3$	25.1 (18.5 $\pm$ 0.1)	11.3 (9.3 $\pm$ 0.4)	10.0 (6.3 $\pm$ 0.5)	28.4 (23.1 $\pm$ 0.1)	6.3 (3.6 $\pm$ 0.2)	6.9 (4.6 $\pm$ 0.2)
NdF $_3$	26.2 (19.1 $\pm$ 0.2)	12.0 (9.3 $\pm$ 0.5)	10.8 (6.5 $\pm$ 0.3)	29.1 (23.8 $\pm$ 0.1)	6.7 (3.8 $\pm$ 0.2)	7.1 (4.9 $\pm$ 0.2)

**Table 7.** Calculated elastic constants for the  $Pnma$  structures.

System	Elastic constants ( $10^{10}$ N m $^{-2}$ )								
	$c_{11}$	$c_{12}$	$c_{13}$	$c_{22}$	$c_{23}$	$c_{33}$	$c_{44}$	$c_{55}$	$c_{66}$
SmF $_3$	20.6	9.1	13.6	24.2	7.7	15.0	4.8	7.8	4.1
EuF $_3$	21.8	9.7	13.6	25.6	7.7	14.9	5.5	9.2	4.5
GdF $_3$	20.2	10.0	12.4	24.8	6.7	15.3	5.4	10.1	4.1
TbF $_3$	19.5	10.1	12.0	24.3	6.4	15.6	5.2	10.5	3.9
DyF $_3$	19.1	10.5	11.9	23.7	6.2	16.9	5.3	11.4	3.8
HoF $_3$	22.7	10.9	13.4	27.8	7.0	16.7	6.8	11.5	5.2
ErF $_3$	20.3	11.0	12.5	24.7	6.4	18.2	6.0	12.2	4.3
TmF $_3$	17.9	10.5	11.8	21.5	5.6	19.2	4.9	12.5	3.5
YbF $_3$	21.6	11.3	13.1	26.1	6.7	18.9	6.8	12.8	5.0
LuF $_3$	19.1	10.5	12.0	22.2	5.3	20.8	5.0	13.4	3.9

where it is seen that in table 4, agreement is better than 2%, while in table 5 it is again around 5%. Also observed, but not given in the tables for space reasons, was noticeable displacement of the F $^-$  shells in the  $Pnma$  structures due to F $^-$  ion polarization.

In table 3, for comparison, calculated lattice parameters using the potentials from [4] are also given when available. In all cases improved agreement with experiment is obtained using the new potentials obtained in this paper, as expected.

In addition, although these properties were not included in the fitting process, elastic constants were calculated for all structures, and these are given in tables 6 and 7. For the  $P\bar{3}c1$  structures the experimental values obtained by Laiho *et al* [18] are also shown in table 6. The calculated values reproduce the general trend of the elastic constants for all four structures, and also predict a value for  $c_{14}$  of  $0.2\text{--}0.3 \times 10^{10}$  N m $^{-2}$ ; much smaller than the other components. This result was also observed by Laiho *et al* [18] who attributed it to a slight anisotropy of the structures giving rise to a value of  $|c_{14}|$  of less than  $0.05 \times 10^{10}$  N m $^{-2}$ .

Table 8 shows the high frequency dielectric constants of the LaF $_3$  to NdF $_3$  structures. Also shown in this table are the experimental values deduced by Laiho *et al* [18]. It can be seen that, although these values have not been used in the fitting procedure, the predicted values are still in good agreement with the experimental ones.

**Table 8.** Calculated high frequency dielectric constants for the  $P\bar{3}c1$  structures, with averaged experimental values for comparison.

System	High frequency dielectric constants		
	$\epsilon_{11}$	$\epsilon_{33}$	$\epsilon$ (exp.)
LaF <sub>3</sub>	2.37	2.35	2.57
CeF <sub>3</sub>	2.42	2.40	2.62
PrF <sub>3</sub>	2.48	2.45	2.63
NdF <sub>3</sub>	2.52	2.48	2.63

**Table 9.** Calculated basic defect and intrinsic defect energies for the rare-earth fluorides (all energies in eV). Also included are the calculated lattice energies ( $E_L$ ) used to calculate the intrinsic defect energies.

RE <sup>3+</sup>	Basic defects				Frenkel				$E_L$
	$V'''_{RE}$	$V_F^\bullet$	$RE_t^{\bullet\bullet\bullet}$	$F'_i$	Anion	Cation	Schottky	Anti-Schottky	
La	53.2462	4.2412	-31.5625	-0.5030	3.74	21.68	16.27	16.63	-49.7011
Ce	53.6750	4.2224	-32.3078	-0.3520	3.87	21.37	16.19	16.79	-50.1538
Pr	49.9847	4.1954	-33.0763	-0.1972	4.00	16.91	11.97	16.93	-50.5960
Nd	50.3971	4.1773	-33.6999	-0.0837	4.09	16.70	11.89	17.09	-51.0398
Sm	49.3368	3.7008	-34.3803	0.7032	4.40	14.96	9.19	18.97	-51.2444
Eu	50.1828	4.0518	-34.9277	1.0473	5.10	15.26	10.10	20.46	-52.2432
Gd	49.6226	4.0336	-35.4297	1.1385	5.17	14.19	9.49	20.22	-52.2377
Tb	49.4112	4.0068	-35.6377	1.1571	5.16	13.77	9.20	20.07	-52.2342
Dy	49.6655	4.0624	-36.4102	1.3375	5.40	13.26	9.00	20.45	-52.8500
Ho	51.2419	4.3373	-35.5878	1.4395	5.78	15.65	10.88	22.10	-53.3740
Er	50.4597	4.2163	-36.5811	1.5151	5.73	13.88	9.64	21.43	-53.4657
Tm	49.5941	4.0708	-37.8007	1.4677	5.54	11.79	8.17	20.24	-53.6332
Yb	51.2703	4.3717	-36.5374	1.6599	6.03	14.73	10.42	22.40	-53.9605
Lu	49.9498	4.1588	-38.4807	1.5821	5.74	11.47	8.17	20.52	-54.2528

## 5. Results: defect properties and intrinsic defect behaviour

Table 9 summarizes the results of defect calculations for the rare-earth fluorides obtained using the new potentials derived in this paper. The following general comments can be made:

- (i) anion Frenkel disorder is predicted for all ReF<sub>3</sub> systems;
- (ii) anion Frenkel and anti-Schottky energies increase with decreasing ionic radius while the Schottky and cation Frenkel energies decrease as the ionic radius decreases;
- (iii) the energy difference between the most probable and the second most probable form of intrinsic disorder in the ReF<sub>3</sub> systems markedly decreases as the ionic radius of the RE<sup>3+</sup> decreases;
- (iv) the second most probable intrinsic defect in the ReF<sub>3</sub> systems is either the Schottky or the anti-Schottky defect for the first two biggest RE<sup>3+</sup> cations (La<sup>3+</sup> and Ce<sup>3+</sup>) but Schottky disorder is predicted in all other cases.

These conclusions may be considered in the context of previous experimental and simulation studies of ReF<sub>3</sub> systems. From Brillouin scattering experiments on LaF<sub>3</sub>, Ngoepe *et al* [19] deduced that conductivity is related to the mobility of F<sup>-</sup> ions via the formation of F<sup>-</sup> vacancies,



and that formation of a superionic phase would depend on the existence of F<sup>-</sup> sublattice disorder [20]. These conclusions are supported by the present calculations, which predict formation of F<sup>-</sup> vacancies and interstitials. Additional agreement comes from a previous computer modelling study of LaF<sub>3</sub> by Jordan and Catlow [21], which also predicted that anion Frenkel disorder would be preferred over Schottky disorder on energetic grounds.

## 6. Conclusions

This paper has shown that the rare-earth fluorides can be accurately modelled using empirically fitted potentials, and that the elastic and dielectric constants can be reliably predicted. Predictions can be made of intrinsic defect behaviour, which agree with available experimental data. The potentials obtained are being further employed in a study of rare-earth doping in BaLiF<sub>3</sub> which is currently in preparation [22].

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## References

- [1] Jackson R A, Valerio M E G and de Lima J F 1996 *J. Phys.: Condens. Matter* **8** 10931
- [2] Valerio M E G, Jackson R A and de Lima J F 1998 *J. Phys.: Condens. Matter* **10** 3353
- [3] Valerio M E G, de Lima J F and Jackson R A 1999 *Radiat. Eff. Defects Solids* **151** 1061
- [4] Corish J, Catlow C R A, Jacobs P W M and Ong S H 1982 *Phys. Rev. B* **25** 6425
- [5] Gale J D 1996 *Phil. Mag. B* **73** 3
- [6] Gale J D 1997 *J. Chem. Soc., Faraday Trans.* **93** 629
- [7] Mott N F and Littleton M J 1938 *Trans. Faraday Soc.* **34** 485
- [8] Catlow C R A 1989 *J. Chem. Soc., Faraday Trans. II* **85** 335
- [9] Fletcher D A, McMeeking R F and Parkin D 1996 *J. Chem. Information Comput. Sci.* **36** 746
- [10] Wyckoff R W G 1964 *Crystal Structures* vol 2, 2nd edn (New York: Wiley)
- [11] Belzner A, Schulz H and Heger G 1994 *Z. Kristallogr.* **209** 239
- [12] Mi J X, Shen J C, Pan B M and Liang J 1996 *DIKEE* **21** 63
- [13] Maksimov B A, Sirota M I, Galiulin R V and Sobolev B P 1985 *Kristallografiya* **30** 284
- [14] Kondratyuk I P, Loshmanov A A, Muradyan L A, Maksimov B A, Sirota M I, Krivandina E A and Sobolev B P 1988 *Sov. Phys.-Crystallogr.* **33** 105
- [15] Bukvetskii B V and Garashina L S 1977 *Coord. Chem.* **3** 1024
- [16] Piotrowski M, Ptasiwicz-Bak H and Murasik A 1979 *Phys. Status Solidi* **55** K163
- [17] Kraemer K, Romstedt H, Guedel H-U, Fischer P, Murasik A and Fernandez-Diaz M T 1996 *Eur. J. Solid State Inorg. Chem.* **33** 273
- [18] Laiho R, Lakkisto M and Levola T 1983 *Phil. Mag. A* **47** 235
- [19] Ngoepe P E, Comins J D and Every A G 1986 *Phys. Rev. B* **34** 8153
- [20] Ngoepe P E and Comins J D 1988 *Phys. Rev. Lett.* **61** 978
- [21] Jordan W M and Catlow C R A 1987 *Cryst. Latt. Defects Am. Mater.* **15** 81
- [22] Jackson R A, Valerio M E G and de Lima J F in preparation