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Electrostatic energy and anion ordering in monoclinic ScOF. By W. W. BARKER, *C.S.I.R.O. Division of Applied Mineralogy, Melbourne, Australia*

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The electrostatic energy for each of the three possible anion configurations consistent with the structural data for monoclinic scandium oxyfluoride has been calculated by the Ewald method. The results support the conclusion of Holmberg obtained from X-ray data as to the actual anion array. In terms of the Born model the calculated values explain why one particular array is favoured over the others.

ScOF is isostructural with the room temperature stable form of zirconium dioxide (baddeleyite) (Table 1). On heating, baddeleyite undergoes a martensitic transformation at about 1250°C to a tetragonal form (Wolten, 1963). In this transformation the oxygen ions in the O(1) sites of Table 1 undergo the major rearrangement, changing the cation coordination number from seven to eight, whereas the ions in the O(2) sites occupy the habit and twinning plane common to the two polymorphs (Wolten, 1964). A theoretical study has been undertaken to determine whether the polymorphism in ZrO₂ can be explained in terms of a simple cohesive energy model. In order to test the validity of the model used it was decided to determine whether the actual anion arrangement found in ScOF could be sufficiently explained in terms of the electrostatic energy contribution to the total cohesive energy. This approach is justified in that the ionic radii and repulsive parameters of the O²⁻ and F⁻ ions are similar (Pauling, 1960) and the atomic positional parameters are sufficiently similar in value for the repulsive forces to differ only slightly from model to model.

Holmberg (1966) in a structural analysis of the compound ScOF analysed the data in terms of three models, each model involving a different arrangement of the anions among the two sets of fourfold position of the space group *P2₁/c*. As shown in Table 1 the positional parameters for the three models are the same within the standard deviations, but the first gives a better fit to the observed data as shown by the lower *R* value and the lower standard deviation.

The electrostatic energy for each model was calculated by a modified Ewald method (Kittel, 1956) developed and programmed by Dr I. D. Campbell of the C.S.I.R.O. Division of Chemical Physics, and the results are shown in Table 2. Madelung constants as such were not calculated

because of the low symmetry and structure dependence of the atomic arrangement, and the seven metal-anion distances in a single cation coordination polyhedron are all different.

The results listed in Table 2 show that the actual anion configuration in monoclinic ScOF leads to the maximum possible value of the electrostatic energy consistent with ordering the two sets of anions as shown in Table 1. The difference between the highest and lowest values calculated is 170 kcal.mole⁻¹ and contributions from other forces operative, such as van der Waals interactions, would be expected to be much smaller than this figure. It is realized that static polarization forces may contribute significantly to the electrostatic energy (Coogan, 1967), but the recorded values of the electronic polarizabilities of the anions (Kittel, 1956) do not seem sufficiently dissimilar in value to account for a difference in energy of 170 kcal.mole⁻¹ between the models listed.

References

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Table 2. *Calculated electrostatic energies for each of the possible anion configurations*

	Model 1	Model 2	Model 3
Electrostatic energy (kcal. mole ⁻¹)	1806 ± 1	1635 ± 1	1702 ± 1

Table 1. *Final atomic parameters, isotropic temperature factors (B), and reliability values (R) in ZrO₂ and ScOF for different fluorine and oxygen arrangements*

	ZrO ₂	ScOF		
		Model 1	Model 2	Model 3
	Zr	Sc	Sc	Sc
<i>x</i>	0.2758 ± 2	0.3073 ± 6	0.3080 ± 7	0.3077 ± 6
<i>y</i>	0.0411 ± 2	0.0267 ± 5	0.0266 ± 6	0.0266 ± 6
<i>z</i>	0.2082 ± 2	0.2129 ± 10	0.2122 ± 13	0.2124 ± 11
<i>B</i> (Å ²)	0.303	0.33 ± 5	0.35 ± 6	0.36 ± 5
	O(1)	F	O	(F, O)
<i>x</i>	0.0703 ± 15	0.0570 ± 18	0.0586 ± 24	0.0578 ± 20
<i>y</i>	0.3359 ± 14	0.3254 ± 15	0.3237 ± 19	0.3243 ± 17
<i>z</i>	0.3406 ± 13	0.3426 ± 31	0.3423 ± 48	0.3441 ± 36
<i>B</i> (Å ²)	0.317	0.8 ± 2	-0.1 ± 3	0.3 ± 2
	O(2)	O	F	(F, O)
<i>x</i>	0.4423 ± 15	0.4574 ± 18	0.4564 ± 25	0.4575 ± 21
<i>y</i>	0.7549 ± 14	0.7525 ± 26	0.7519 ± 34	0.7519 ± 29
<i>z</i>	0.4789 ± 13	0.4900 ± 26	0.4949 ± 34	0.4906 ± 28
<i>B</i> (Å ²)	0.229	0.4 - 2	1.6 - 3	1.0 - 2
<i>R</i>	8.6%	7.6%	9.5%	8.2%