

The form of  $p(\eta, T)$  obtained in the previous section [Eq. (10)] is verified by the plots in Figs. 3(a)–3(c). The validity of Eq. (5) for  $\tau_{\text{enc}}$  is assumed. The simple unimolecular reaction model is thus seen to account in a satisfactory way for the exchange probability parameter  $p(\eta, T)$ . Interestingly enough, it is empirically found that  $J_0\tau_{\text{enc}}$  for radical–radical exchange is strongly solvent-dependent, and that for the same solvent (methyl cyclohexane)  $J_0\tau_{\text{enc}} \gg J_0'\tau'_{\text{enc}}$ . The values of  $J_0\tau_{\text{enc}}$  are found to be  $1.01 \times 10^3 \eta/T$  (*n*-pentane),  $2.81 \times 10^3 \eta/T$  (propane),  $\approx 1 \times 10^3 \eta/T$  (methylcyclohexane), while  $J_0'\tau'_{\text{enc}} = 0.19 \times 10^3 \eta/T$  (methylcyclohexane). Viscosities are expressed in centipoise.

From the empirical values of  $J_0\tau_{\text{enc}}$  and Eq. (5) with  $\lambda = 3 \times 10^{-8}$  cm,  $J_0$  was calculated to be  $1.6 \times 10^{11}$  sec<sup>-1</sup> in *n*-pentane,  $4.5 \times 10^{11}$  sec<sup>-1</sup> in propane and  $\approx 1.6 \times 10^{11}$  sec<sup>-1</sup> in methylcyclohexane.  $J_0'\tau'_{\text{enc}}$  is

about an order of magnitude smaller than the corresponding quantity for radical–radical exchange. It is expected, however, that  $\lambda'$ , the interaction radius for the oxygen molecule, is also appreciably smaller. These values of  $J_0$  are about an order of magnitude larger than the value estimated by Pake and Tuttle<sup>2</sup> for polycrystalline DPPH ( $10^{10}$ – $10^{11}$  sec<sup>-1</sup>).

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ZrF<sub>6</sub><sup>4-</sup> ion and bond distances

A single crystal melt of stoichiometric ZrF<sub>4</sub> used in these analyses indicated this Hf:Zr ratio. X-ray precession showed a tetragonal unit cell with  $a = 0.02$ ,  $c = 18.62$ ; space group  $I4_1/amd$ . However, an electron density map obtained by a method of volumes of the unit cell from which  $\rho = 3.06$  g cm<sup>-3</sup>.

Photograph of the  $hkl$  reflections obtained by visual comparison with the range of the values.

The  $\text{CuK}\alpha$  line is 139 cm<sup>-1</sup>. The 0.01 cm parameter is larger than that in the errors were corrected for them was applied to the relative structure scale was four

#### STRUCTURE

The beryllium symmetry to Group  $I4_1/amd$ , not wholly in the method, together with atomic contributions permitted the presence from electron

<sup>7</sup> A. J. C. Wilson, *International Tables for X-ray Crystallography*, Birmingham Press, Birmingham, 1952.  
<sup>8</sup> All Fourier transforms were done with the program FOR-DAP-2 written by R. D. Ellis

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### Crystal Structure of Li<sub>6</sub>BeF<sub>4</sub>ZrF<sub>8</sub>†

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The crystal structure of Li<sub>6</sub>BeF<sub>4</sub>ZrF<sub>8</sub> has been determined by x-ray diffraction. The tetragonal unit cell, having  $a = 6.57$ ,  $c = 18.62$  Å, contains four formula weights; the space group is  $D_{4h}^{19} - I4_1/amd$ . Discrete BeF<sub>4</sub><sup>2-</sup> and ZrF<sub>6</sub><sup>4-</sup> ions are connected by shared Li<sup>+</sup> ions. The BeF<sub>4</sub><sup>2-</sup> tetrahedron is quite regular with a Be–F distance of  $1.57 \pm 0.01$  Å; the ZrF<sub>6</sub><sup>4-</sup> dodecahedron has two independent Zr–F bonds of  $2.05 \pm 0.01$  Å and  $2.16 \pm 0.01$  Å, and deviates considerably from the shape predicted by theory.

#### INTRODUCTION

ZIRCONIUM is known to occur as the central atom of a variety of complex coordination polyhedra, often bearing eight ligands arranged in dodecahedral or square-antiprismatic symmetry.<sup>1,2</sup> Racah<sup>3</sup> and Duffey<sup>4</sup> have derived orbital strengths for these configurations using  $d^4s^3p^3$  hybridization. Their calculations established no significant energy difference between the configurations, if isolated complexes are considered.

The configuration adopted in a particular crystal is therefore determined in part by external influences, such as ligand–ligand repulsions, constraints due to

bonding between ligands, and packing requirements. Thus it is interesting to examine  $MX_8$ -type configurations in which, as in the well known  $\text{Mo}(\text{CN})_8^{4-}$  ion,<sup>5</sup> the central metal atom is bonded to eight apparently equivalent monodentate ligands.

In an investigation of the phase diagram of the ternary system LiF–BeF<sub>2</sub>–ZrF<sub>4</sub>, Thoma *et al.*<sup>6</sup> discovered a primary phase of composition  $6\text{LiF} \cdot \text{BeF}_2 \cdot \text{ZrF}_4$ . The stoichiometry and preliminary x-ray studies suggested the possible occurrence of complex octafluorozirconate and tetrafluoroberyllate ions in the crystal.

The coexistence of two discrete complex anions in a crystal is not common. But since it seemed likely in this compound, a crystal-structure analysis was carried out to examine in detail the configuration of the discrete

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<sup>2</sup> R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *Nature* **199**, 559 (1963).

<sup>3</sup> G. Racah, *J. Chem. Phys.* **11**, 214 (1943).

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<sup>5</sup> J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.* **61**, 2853 (1939).

<sup>6</sup> R. E. Thoma *et al.*, U.S. Atomic Energy Commission Report ORNL-3591 (1964), pp. 3 ff.