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The crystal structure of β -KCeF₄*. By George Brunton, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

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The crystal structure of β -KCeF₄ has been determined by X-ray diffraction. The space group is *Pnma*, $a_0 = 6\cdot2895 \pm 0\cdot0003$, $b_0 = 3\cdot8040 \pm 0\cdot0003$, $c_0 = 15\cdot596 \pm 0\cdot002$ Å. The structure consists of a three-dimensional framework of 9-coordinated Ce-F and K-F polyhedra.

Alkali metal complexes with the rare earth fluorides are being studied because of their relationship to the corresponding actinide elements which are of interest to molten salt breeder reactor technology. Cerium is analogous in its properties to plutonium and a preliminary study of the

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation. phase relationships in the system KF-CeF₃ (Barton, Brunton, Hsu & Insley, 1967) showed that there are two stable phases of KCeF₄: α -KCeF₄, fluorite-cubic and β -KCeF₄, orthorhombic.

 β -KCeF₄ is the first polymorph of orthorhombic symmetry which has been described. Zachariasen (1948*a*, *b*) described compounds β_1 -KLaF₄ and β_1 -KCeF₄ and reported them to be isostructural with β_1 -K₂UF₆ which has P62*m* symmetry. Sears (1967) has determined the crystal structure

Table 1. Atomic parameters for β -KCeF₄

| | x | У | Z | β_{11} | β22 | β_{33} | β_{12} | β_{13} | β_{23} |
|-------------|---------------|------|---------------|---------------|------------|---------------|--------------|---------------|--------------|
| Ce | 0.25105 (0.4) | 0.25 | 0.43765 (0.2) | 0.00338 (0.8) | 0.0077 (2) | 0.00072 (0.1) | 0.0 | -0.00002(0.1) | 0.0 |
| K | 0.2766 (3) | 0.75 | 0.20178 (0.9) | 0.0046 (2) | 0.0250 (8) | 0.00104 (0.4) | 0.0 | 0.00008 (0.7) | 0.0 |
| F(1) | 0.1376 (6) | 0.25 | 0.0364 (3) | 0.0060 (7) | 0.020 (30) | 0.0015 (2) | 0.0 | 0.0004 (3) | 0.0 |
| F(2) | -0.0053 (6) | 0.75 | 0.4406 (2) | 0.0062 (8) | 0.018 (30) | 0.0009 (2) | 0.0 | 0.0002(2) | 0.0 |
| F(3) | 0.3970 (7) | 0.75 | 0.3638 (3) | 0.0095 (8) | 0.010 (20) | 0.0013 (2) | 0.0 | 0.0008 (3) | 0.0 |
| F(4) | 0.0849 (7) | 0.22 | 0.3044 (3) | 0.0131 (9) | 0.015 (20) | 0.0012 (2) | 0.0 | -0.0003 (3) | 0.0 |

* Coefficients in the temperature factor; exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The number in parentheses is $\sigma \times 10^4$.



Fig. 1. The contents of one unit cell (outlined) of β -KCeF₄ tilted 45° around a_0 .

of β_1 -KLaF₄ and has shown that it is not isostructural with β_1 -K₂UF₆ as had been proposed. Sears shows that the space group for β_1 -KLaF₄ is $P\delta$, that one of the cation positions is statistically occupied by 0.5K⁺ and 0.5La³⁺, and that there is statistical occupation of two of the F⁻ positions.

Zachariasen's β_1 -KCeF₄ does not occur as an equilibrium compound and has not been re-examined.

Experimental

Single crystals of β -KCeF₄ were grown as the primary phase from a melt having the composition 35 mole % KF, 65 mole % CeF₃. At the stoichiometric composition, β -KCeF₄ becomes fluorite-cubic α -KCeF₄ above 755°C. Fragments of the crystals were ground to approximately spherical shape in an air-driven race and an ellipsoid of dimensions 0.182 by 0.252 by 0.234 mm was selected for single-crystal diffraction. The intensities of the reflections were measured with a computer-operated Picker fourcircle goniostat and a scintillation-counter detector using unfiltered Mo $K\alpha$ radiation ($K\alpha_1 = 0.70926$ and $K\alpha_2 =$ 0.713543 Å). Twelve hundred and seventy nine independent reflections out to $80^{\circ} 2\theta$ were measured by the 2θ scan technique. The linear absorption for Mo $K\alpha$ radiation by β -KCeF₄ is 13.396 mm⁻¹ and an absorption correction was calculated for each reflection.

Refinement and results

The observed conditions for diffraction, *hkl*: no conditions, 0kl: k+l=2n, and hk0: h=2n, are consistent with the space group Pnma. The lattice parameters were refined as part of the set up procedure on the X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). Twenty nine additional high angle reflections were measured at plus and minus 2θ and the final least-squares results for the lattice parameters are: $a_0 = 6.2895 \pm 0.0003$, $b_0 = 3.8040 \pm 0.0003$ and $c_0 = 15.596 \pm 0.002$ Å. The calculated density is 4.5424 g.cm⁻³ and Z=4. The reflections were corrected for Lorentz-polarization factors and for absorption and a three-dimensional Patterson was calculated from these data All of the atoms in the asymmetric unit are at special position 4(c) with y = 0.25. The x and z positional parameters and the anisotropic temperature factors were refined using a modification of the Busing, Martin & Levy (1962) leastsquares computer program. The quantity $\Sigma w(F_o - F_c)^2$ was minimized with weights, w, equal to the reciprocals of the variances which were estimated from the empirical equation: $\sigma^2(F_a^2) = s(T + B + 0.0036(T - B)^2)/(Lp)^2$, where s =scale factor, T = total, B = background count, and Lp =

Lorentz-polarization correction. Scattering factors for K⁺, Ce³⁺ and F⁻ were taken from Cromer & Waber (1965) and the values of $\Delta f' = -0.3$ and $\Delta f'' = 3.0$ electrons were taken for the anomalous dispersion of Mo K α radiation by

Table 3. Observed and calculated structure factors for β -KCeF₄

85488870922579531579531579545482401888502601513264115877-19231 FCALL L 112399200156 -694799200156 -694799200156 -6947991253459036252 -11055459036252 -11055459036252 -1123915 -239254 9 59 0 0 9 9 9 9 9 7 57 15 3 8 16 10 6 4 59 0 20 0 2 4 53 0 02822348509183856569*02225268828992314 27887555039577919016118805020180891757 177919016118805020180891757 ันชาติเหล่านั้นนั้นสื่อสันธิมชันชันต่านี้ไว้กุนธารครั้งส่อร้อ ใหาริงชือธายันชื่อชื่อสัปชาส เชอชมร์นะได้ พ.พ.พ.ศ. 1944 - พ.ศ. 1945 พ.ศ. 1945 - พ. น้เห็นอันธุณร์นั้น 2010 ในข่ายใช้เป็นให้เป็นขึ้นได้เป็นประสาชกับให้เข้าใช้. ที่เป็นขึ้น และมีปลังห์มีเส็นสุขานส นายาว ใช้พิชันหายและกระแกกลอดเห็นให้เป็นสีข้ายสุขากกลอดเป็นสีข้ายเป็น เป็นกลอดเป็นไป เป็นที่มีสีขึ้นที่เป็นสีขาม 234567890112345678901123456789221 1234567 80%%%881%%208 113151719223227 ส่งประการส่วนสารที่ก่านการประสารสราชการประการประการประการประการประการประการประการประการประการประสาร ส่งประการประการประการประการประการประการประการประการประการประการประการประการประการประการประการประการประการประการ ៰ ៙៙៰៱៝៸៳^៰៲៶៝៸៴៰៲៲៶៰៱៲៰៲៲៲៲៲៶៸៶៶៷៷៰៱៸៰៲៶៲៰៰៹៓៸៱៷ឨ៙ឨ៸៰៲៶៰៷៶៰៸៰ឣ៴៷៰ឩ៰៲ៜ៲៸៷៓៲៲៰៰៸៸៵៲៵ៜ៲៷៲៲៹៲៶៲៵៰៶៸៴៵៶ឩ៰៶៰**ឣ** -38-3-6-77 1.239522612336581211407533871249W 43380763313845882655245615102 508565437579942658222773980649209711268972112688665857-66-77 487868688658557-66-77 135791135791225 0123456789011234567890 2 6 8 10 2 14 16 18 20 20 278032267848815869355311507121327725551711081906516 01234567890123456789 0-23 4567 8901123 1567 8922222 L203113507699220875920207 2 115875-155727144005-121-3287107 -3 129 13 210 -27 55 58 17 11 -108 -18 -18 -18 -16 -15 1234567890112 9 10 11 12 13 14 15 - 76 J2

Table 2. Interatomic distances for β -KCeF₄

| Ce-F(4) | 2·326 (4) Å | K-F(3) | 2∙587 (5) Å |
|-----------------|-------------|--------------|-------------|
| 2[Ce-F(3)] | 2.406(3) | K-F(2) | 2.611 (4) |
| $\dot{C}e-F(2)$ | 2.448 (4) | K-F(3) | 2.639 (5) |
| Ce-F(1) | 2·465 (4) | 2[K-F(4)] | 2.717 (3) |
| 2[Ce-F(2)] | 2.494 (3) | 2[K-F(4)] | 2.763 (4) |
| 2[Ce-F(1)] | 2.546 (4) | 2[K-F(1)] | 3.321 (4) |
| F(1) - F(3) | 2.701 (6) | F(1) - F(2) | 2.753 (6) |
| 2[F(1)-F(1)] | 2.812 (6) | 2[F(1)-F(3)] | 2.885 (5) |
| 2[F(1) - F(2)] | 2.965 (5) | 2[F(2)-F(2)] | 2.655 (5) |
| F(2) - F(3) | 2.800 (6) | 2[F(2)-F(4)] | 2.907 (4) |
| 2[F(3)-F(4)] | 2.887 (5) | | |

Table 3 (cont.)

| | 682 692 692 692 692 692 692 692 692 692 69 | L 1 2 3 4 5 5 7 8 9 10 11 2 1 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 1 2 3 4 5 5 7 7 8 9 10 11 2 1 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 5 7 7 8 9 10 11 2 3 4 5 7 7 8 7 10 11 11 11 11 11 11 11 11 11 11 11 11 | R_21162-762-1786-673-1156-77-119758-11-5-1456-68-7516-7234-752-975-1-5-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-1-5-1456-68-7516-7234-752-975-10-752-975-10-75-1456-68-7516-7234-752-975-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752-10-752- 1-5-1456-1456-1456-1456-1456-1456-1456-1 | 1985 1977 12 5 4 5 5 5 7 6 19 7 0 7 7 7 19 18 5 5 7 7 8 19 0 7 19 7 7 7 19 19 7 7 19 19 7 7 19 19 19 19 19 19 19 19 19 19 19 19 19 | F085 | L FORS 5 6 7 98 5 7 98 5 8 6 7 98 5 8 99 5 8 | | 8851-9-134659-980-980-980-9910-9910-9910-9910-9910-9 | F085 FC 18 - 18 - 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | AL 1917 - 2-5 - 2-7 - 2-5 - 2-5 - 2-2 - 2-1 - 2-5 - 2- | نْنَانَ رَحْتَانَ مَعْتَدَةً مَنْ الْمَنْعَجَمَة مَنْ الْمَنْعَجَمَة مَنْ الْمَنْ الْمَعْجَمَة الْمَنْ الْمَعْ مَنْ الْمَعْدَمَة مَنْ الْمَنْعَانَ الْمَنْ الْمَنْ الْمَنْ الْمَنْ الْمَنْ الْمَنْ الْمَنْ الْمَنْ الْمَنْ ال مَنْ الْمَنْ الْ مَنْ الْمَنْ الْمَا لَالْمَا الْمَنْ الْمَنْ الْمَنْ الْمَا الْمَالْيَا الْمَنْ الْمَا الْمَالْيَ الْمَالْمَ الْمَالْيَا الْمَا الْعَالَيْلَ الْعَالَيْلَ الْمَالْيَا الْلَيْلَ الْلَيْلَ الْلَالْيَا الْمُ | |
|----------------|--|--|--|--|---|---|--|--|---|--|---|--------|
| 10112131451617 | 34 36 9 9 7 -6 14 -44 0 0 57 -56 6 5 L 7 0 | 21 5 22 37 2 87 2 87 3 0 4 22 5 21 5 6 7 98 | 4 19 -35 20 1 L -35 2 -29 3 -22 5 -22 5 8 6 95 7 | 0 -1 49 49 7 3 L 72 72 8 -2 26 26 17 16 19 -19 5 -6 79 -78 | 6 5 7 56 5 8 8 0 1 0 105 10 1 21 -2 2 70 6 3 5 4 7 5 13 - | N 1 11 8 2 6 7 3 1 2 5 1 0 6 7 1 6 7 1 6 7 1 3 9 3 3 10 5 | 18 -59 2 +1 5 7 -2 10 5 3 11 5 7 8 9 1 5 7 8 5 7 8 -6 5 5 3 | 0 -5 3 62 -61 4 5 4 5 4 3 -42 6 9 0 L 8 9 0 L 8 9 0 L 8 9 0 L 8 9 11 11 7 7 72 12 | 10 69 16 40 16 8 0 44 4 | -9 10 41 -66 11 5 16 12 0 -40 13 12 -14 10 1 2 0 12 5 1 28 45 2 9 4 3 67 59 4 7 | 40 6 44 44 7 7 0 -1 11 11 -12 1 52 44 1 2 3 20 -24 29 4 9 -1 11 5 22 2 64 6 13 1 -5 | 910834 |

cerium [Dauben & Templeton (1955)]. The positional parameters and anisotropic temperature factors are listed in Table 1. The discrepancy index $R = \Sigma ||F_0| - |F_0||/\Sigma |F_0| = 0.0433$. The standard deviation of an observation of unit weight= $[\Sigma w(F_o - F_c)^2/(n_o - n_v)]^{1/2} = 1.5688$ where n_o is the number of reflections and n_v the number of variables.

Table 2 contains a list of the interatomic distances and Table 3 contains the observed and calculated structure factors. Fig.1 is a stereoscopic pair of drawings showing the contents of approximately one unit cell of β -KCeF₄ tilted 45° about a_0 . The structure consists of a threedimensional framework of 9-coordinated Ce–F and K–F polyhedra. One of these polyhedra can be described as having 6F⁻ ions at the corners of a trigonal prism and 3F⁻ each at the apex of a pyramid on each of the prism faces. The basal triangular faces of the K⁺ polyhedra are shared with other K⁺ polyhedra are shared with edges of Ce³⁺ polyhedra which also share edges with each other to form a simple framework structure.

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The crystal and molecular structure of strontium tartrate trihydrate. A correction. By G.K.AMBADY, Centre of Advanced Study in Biophysics and Crystallography, University of Madras, Madras 25, India

(Received 4 November 1968)

A corrected value for one atomic coordinate is given.

In Table 3 of a recent article (Ambady, 1968) the incorrect value 0.6787 is given for the y coordinate of atom C(3). The correct value is 0.6687.

Reference

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