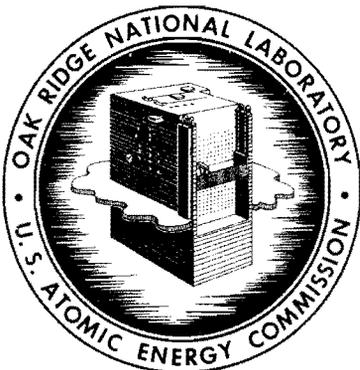


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X-RAY DIFFRACTION STUDY OF Cs_3ZrF_7

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ABSTRACT

A single-crystal X-ray diffraction study of Cs_3ZrF_7 was made, in which the unit-cell dimensions and probable space groups were determined and the metal-ion positions deduced. The face-centered cubic unit cell has $a = 9.70 \pm .02\overset{0}{\text{A}}$, and the space group is $F\bar{4}3m$, $F432$ or $Fm3m$. The metal ions lie on or near the following positions: Zr^{4+} at $(0,0,0) + \text{face-centering}$ and Cs^+ at $(1/2,1/2,1/2; 1/4,1/4,1/4; 3/4,3/4,3/4) + \text{face-centering}$; but the fluoride-ion arrangement is disordered. This compound is apparently isotypic with K_3ZrF_7 , $(\text{NH}_4)_3\text{ZrF}_7$, and K_3UF_7 as regards the metal ions, but no comparison can be made from this work as to the exact arrangement of the fluoride ions. The X-ray powder pattern is given for use in identification.

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I. INTRODUCTION

A survey of the phase diagrams of many alkali fluoride-tetravalent metal fluoride systems¹ shows that the majority of them have a congruently-melting 3:1 compound. The X-ray diffraction work on $3\text{CsF}\cdot\text{ZrF}_4$ described here is part of an analysis of the structures of this class of compounds, and also part of a determination of the phase diagram of the $\text{CsF}\text{-ZrF}_4$ binary system.²

II. PREPARATION OF CRYSTALS

Single crystals of Cs_3ZrF_7 were prepared from a melt composed of CsF and ZrF_4 mixed in a 3:1 mole ratio. The components were purified of hydrolysis products by treatment with ammonium bifluoride.

During heating and cooling, the sample was protected by an atmosphere of purified helium. Contamination by moisture was held to a minimum during unloading by removing the sample from the furnace at approximately 300°C and placing it in a dry box. The single crystals of Cs_3ZrF_7 obtained from this melt were protected from moisture during optical examination and loading into glass capillaries for X-ray study by immersion in a bath of mineral oil.

III. UNIT-CELL AND SPACE-GROUP DETERMINATION

Single-crystal photographs taken with the Buerger precession camera provided data for determination of the unit-cell dimensions and the diffraction symmetry.

The crystals are face-centered cubic with $a_0 = 9.70 \pm .02 \text{ \AA}$. The density is not easily measured, so an estimate of 4.62 g cm^{-3} was made by assuming that the molar volumes of 3CsF and 1ZrF_4 are additive in the compound.³ From this approximation it is obvious that there are 4 formula weights per unit cell; the X-ray density is 4.53 g cm^{-3} .

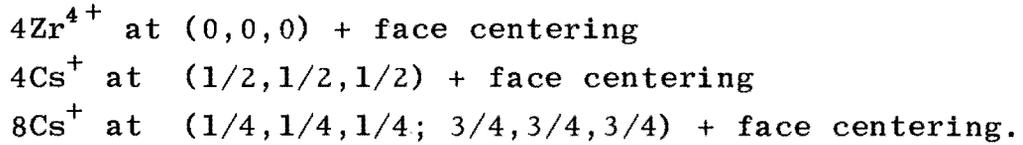
Precession photographs of the $0kl$, $1kl$, $2kl$, and hhl zones showed the diffraction symmetry $m3mF \dots$. The probable space group is thus $F\bar{4}3m$, $F432$, or $Fm3m$.

IV. LOCATION OF THE IONS

A consideration of the possible sites for locating 12 cesium and 4 zirconium ions in the unit cell shows that they may occupy the various 4-fold and 8-fold equivalent positions of either of the three space groups mentioned above. However, once these ions are placed, there is no combination left in either space group which will provide sites for the 28 fluoride ions. Thus, it is concluded, as was done previously by Hampson and Pauling⁴ for $(\text{NH}_4)_3\text{ZrF}_7$ and K_3ZrF_7 and by Zachariassen⁵ for K_3UF_7 , that there is some randomness in the structure of Cs_3ZrF_7 . Moreover, the metal ions may not lie exactly on these 4-fold and 8-fold positions, but may be also statistically distributed over positions of higher multiplicity.

No attempt was made to obtain accurate intensity measurements with these crystals, but a survey of the intensity

relationships on the films and space-group requirements indicate that the metal ions must lie on or near the following sites:



In addition to the systematic absences due to the face centering, the $0k\ell$ reflections are strong only for $k+\ell = 4n$ while those reflections with $k+\ell = 4n+2$ are observable only after long exposure. Although this type of absence is usually indicative of a d-glide plane (or an approximation to one), it arises from another cause in this crystal. If only the heavy-atom contribution to the scattering is considered, the structure factor expression reduces, for atoms in the above positions, to:

$$\begin{aligned}
 F_{0k\ell} &\sim f(\text{Zr}^{4+}) + 3f(\text{Cs}^+), \quad k+\ell = 4n \\
 F_{0k\ell} &\sim f(\text{Zr}^{4+}) - f(\text{Cs}^+), \quad k+\ell = 4n+2.
 \end{aligned}$$

The similarity in scattering power of Zr^{4+} and Cs^+ makes the second expression quite small, thus explaining the near absences.

Because of the disorder in the arrangement of the fluoride ions, they cannot be located in a straightforward way; but a reasonable configuration may be assumed and the resulting X-ray intensities compared with observation. In the case of K_3ZrF_7 (and $(\text{NH}_4)_3\text{ZrF}_7$) and in K_3UF_7 , a ZrF_7^{\equiv} and a UF_7^{\equiv} ion, respectively, was assumed to exist;^{4,5}

and the structures were reported to contain these complex ions randomly distributed over a set of plausible orientations. While the Cs_3ZrF_7 structure appears to be, at least approximately, isomorphous with these crystals, it is not possible to say from our data what the orientation of the ZrF_7^{\equiv} is, or whether the metal ions are slightly displaced from the sites given above. To answer these questions, very precise X-ray intensities would be needed; and it does not seem feasible at present to obtain crystals of Cs_3ZrF_7 of suitable quality to provide these data.

A powder diagram of Cs_3ZrF_7 was made with a Debye-Scherrer camera and CuK_α radiation. The indexed pattern is given in Table I for use in identification of the compound. The lines having indices k, ℓ , where $k+\ell = 4n+2$ were unobservable because of reasons discussed above.

The single-crystal photographs of Cs_3ZrF_7 showed superposed diffraction patterns from single crystals of a second phase. The Bragg angles of these diffraction spots agreed with the powder pattern of Cs_2ZrF_6 . Moreover the reciprocal lattice of this second phase showed a definite axial relationship to the Cs_3ZrF_7 lattice and was twinned, suggesting that the Cs_2ZrF_6 arose from some decomposition of the Cs_3ZrF_7 , perhaps on cooling. Single crystals of Cs_2ZrF_6 of sufficient size for X-ray study are not yet available, so the structural relation between these two phases is not known.

Table I.

X-ray Powder Pattern of Cs_3ZrF_7

<u>hkl</u>	<u>d(Å)^o obs.</u>	<u>d(Å)^o calc.</u>	<u>I obs.</u>
220	3.43	3.43	vs
311	2.92	2.92	vw
222	2.803	2.799	vw
400	2.424	2.424	s
422	1.980	1.989	s
440	1.715	1.714	m
620	1.535	1.533	ms
642	1.297	1.296	ms

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