CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712
AND OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

The Crystal Structure of $Cs_4Mg_3F_{10}$[1]

BY H. STEINFINK AND GEORGE BRUNTON

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The compound $Cs_4Mg_3F_{10}$ crystallizes in space group Cmca with $a_0 = 6.1333$ (3), $b_0 = 14.561$ (2), and $c_0 = 13.653$ (1) Å. The observed density is 4.0 ± 0.4 g/cm^3 and the calculated density is 4.3276 g/cm^3; $Z = 4$. The structure consists of corrugated sheets of linked MgF_6 octahedra parallel to (010) with the sheets held together by the Cs^+ ions. The basic unit within a corrugated sheet consists of three octahedra in which the central octahedron shares two opposing faces with the other two octahedra. The basic units are linked by the outside octahedra of each unit sharing corners with the outside octahedra of other basic units. The Mg^{2+}–F^- distances vary from 1.890 to 2.104 Å. The Cs^+–F^- distances vary from 2.940 to 3.471 Å.

Introduction

The use of molten salts, in particular fluorides of the heavy metals in conjunction with alkali and alkaline earth fluorides, as working fluids in the molten salt breeder reactor program has led to an extensive investigation of the phase diagrams of such systems. As part of this program, the binary system CsF–MgF_2 is being investigated and it was observed that well-formed, euhedral crystals grew in an ingot of the composition 50 mol % CsF–50 mol % MgF_2. X-Ray diffraction powder patterns of this mixture and optical petrographic examination of the ingot products showed the presence of MgF_2 and of an additional phase which was not the known tetragonal compound $CsF \cdot MgF_2$.[2] Single crystals of this unknown phase were selected from the ingot for crystal structure analysis in order to elucidate its stoichiometry and structural parameters.

Experimental Section

Optical examination of a single crystal showed it to be biaxial with the indices $n_x = 1.454$, $n_z = 1.462$, and $2V = 50°$. Weissenberg and precession photographs were obtained from a well-formed, acicular crystal; the diagrams had diffraction symmetry mmm and extinctions were observed for hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. The space groups C2ca (41) and Cmca (64) are consistent with the diffraction data, and the preliminary lattice constants obtained from the photographs were $a = 6.11$ Å, $b = 14.58$ Å, and $c = 13.64$ Å.

The density of the material was determined using a Berman balance. Several well-formed crystals with a combined weight of approximately 3.5 mg were used and from the weight loss in benzene the density was found to be 4.0 ± 0.4 g/cm^3. The number of formula weights consistent with this density for the compositions xCsF·yMgF$_2$ (x:y = 2:1, 3:2, 4:3, and 5:4) were calculated and it was apparent that the 2:1 and 4:3 compositions were likely stoichiometries consistent with the crystal system and space groups. The 4:3 composition was especially probable because it is close to the 50–50 mol % mixture. For either possibility the unit cell contains 16 Cs^+ which primarily would determine the scattered intensities. It was also observed that the $h0l$ diffraction diagram had very strong diffraction spectra when $l = 4n$ and the spectra were either absent or extremely faint for $l \neq 4n$. The decrease in the $h0l$ intensities was clearly due to the decrease of the scattering factors of the atoms with $(\sin \theta)/\lambda$, indicating that at least the Cs^+ positions and probably several other atoms have x parameters near 0 and that the z parameters have a relationship of z and $^1/_4 - z$ for some of the crystallographically independent atoms.

A single crystal was selected, ground in a Bond grinder to an ellipsoidal shape, with axial dimensions 0.136 × 0.158 × 0.104 mm, and placed on a Picker four-circle automatic single-crystal diffractometer for the collection of three-dimensional X-ray diffraction intensities. Lattice constants were determined from a least-squares refinement of precise 2θ measurements from 32 Mo Kα reflections having values between 43 and 72°, yielding $a = 6.1333$ (3), $b = 14.561$ (2), and $c = 13.653$ (1) Å (λ 0.70926 Å).[3] Diffraction intensities were collected to a value of $2\theta = 80°$; 2040 independent reflections were measured of which 1797 were greater than $\sigma(F_o)$. Integrated intensities were collected using unfiltered Mo Kα radiation measured with a scintillation-counter detector. An angular scan range of 1.35° was step scanned in increments of 0.01° with 0.5-sec counts at each step, and the background was measured on each side of the peak for 20 sec.[3] The data were corrected for Lorentz–polarization effects and for absorption ($\mu = 12.36$ mm^{-1}). The equations

$$\sigma^2(F_o^2) = [T + B + [0.10(T - B)]^2]/A(\mathrm{Lp})^2$$

$$\sigma(F_o) = \sigma(F_o^2)/2F_o$$

were used to estimate the variance for the structure factors where T is the total count, B is the background count, A is the absorption correction, and Lp is the Lorentz–polarization expression. A standard reflection, (008), was used throughout the data gathering to check on intensity drift. One measurement of the standard intensity was assigned unit value and all others were expressed as fractions of this value. The intensities obtained between two successive measurements of the standard reflection were multiplied by the appropriate fraction so that all measured intensities were referred to a single value of the (008) intensity.

Structure Determination

The direct method for the determination of phases was used in the solution of the structure. A Wilson plot was constructed which provided an approximate scale factor and also indicated a centric distribution of intensities so that the space group Cmca was chosen. A program written by Dewar[4] making use of the symbolic addition method yielded a sufficient number of signed $E(hkl)$'s so that the first calculated E map displayed peaks which could be identified as Cs^+, and they were in the 8f positions of the space group with the z

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] G. D. Brunton, H. Insley, T. N. McVay, and R. E. Thoma, ORNL Report 3761, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[3] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Report ORNL 4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1968.

[4] R. Dewar and A. Stone, University of Chicago, personal communication, 1966.

TABLE I

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $Cs_4Mg_3F_{10}$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs_1	0	2542 (0.4)	3939 (0.4)	86 (1)	15 (0.2)	28 (0.3)	0	0	−3 (0.2)
Cs_2	0	4482 (0.3)	1389 (0.3)	72 (0.1)	15 (0.2)	16 (0.2)	0	0	−0.8 (0.1)
Mg_1	0	1170 (2)	1575 (2)	57 (5)	8 (0.8)	12 (1)	0	0	0 (0.7)
Mg_2	0	0	0	48 (7)	10 (1)	11 (1)	0	0	−0.3 (1)
F_1	2100 (6)	958 (2)	403 (2)	61 (7)	19 (1)	17 (1)	−6 (2)	9 (3)	−2 (1)
F_2	2500	1098 (4)	2500	74 (10)	19 (2)	19 (2)	0	−15 (4)	0
F_3	0	4732 (4)	3575 (3)	107 (12)	15 (2)	16 (2)	0	0	3 (2)
F_4	0	2465 (4)	1482 (5)	126 (15)	14 (2)	38 (4)	0	0	7 (2)

[a] The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

parameter relationships as expected on the basis of the $h0l$ diffraction intensities. Additional peaks consistent with Mg^{2+} and F^- were present but it was difficult to decide the particular ionic species from the peak heights. From the Cs^+ positions of the E map, a set of structure factors was calculated, and the signs from this calculation were used in the construction of a three-dimensional electron density map which then yielded peaks that could be unequivocally assigned to Mg^{2+} and F^- and fixed the stoichiometry at the 4:3 composition. The structure was refined by a least-squares procedure using the XFLS program, a modification of ORFLS;[5] the structure factors were weighted by $1/\sigma^2$, and the final R with anisotropic temperature factors is 0.075 and 0.0785 for weighted R. The value of R for the 1797 reflections greater than $\sigma(F_o)$ is 0.0617, and weighted R is 0.0782. The standard deviation of an observation of unit weight is 0.988. The scattering factors used for all atoms are those published by Cromer and Waber;[6] the Cs^+ scattering was corrected for the real ($\Delta f'$) and imaginary contributions ($\Delta f''$).[7] The final atomic parameters and anisotropic temperature factors are shown in Table I, and the set of calculated and observed structure factors scaled to absolute values is listed in Table II. A three-dimensional difference electron density function was calculated with this last set of parameters, and no physically significant peaks were observed. The largest height of the random peaks was $\pm 4\ e^-/Å^3$.

After the stoichiometry had been determined from the structure, ingots with the CsF:MgF_2 compositions of 1:1, 2:1, and 4:3 were prepared. The 1:1 ingot again was a mixture of $Cs_4Mg_3F_{10}$ and MgF_2. The 2:1 ingot was a mixture of CsF and $Cs_4Mg_3F_{10}$. The 4:3 ingot was almost all $Cs_4Mg_3F_{10}$ but not free enough from other phases to warrant chemical analysis. The exact melting behavior of $Cs_4Mg_3F_{10}$ has not been determined and the studies of the CsF–MgF_2 phase equilibria are incomplete.

Discussion

The structure of $Cs_4Mg_3F_{10}$ consists of corrugated sheets of linked MgF_6 octahedra parallel to (010) and is illustrated in Figure 1. The basic unit within a corrugated sheet consists of three octahedra where the central octahedron shares two opposing faces with two other octahedra. Each end octahedron within this unit of three thus shares one face with the central octahedron and corners with two octahedra which in turn are part of two separate units of three. The sheets are held together by the Cs^+, and the pronounced cleavage perpendicular to the (010) reflects the weaker bonding. The Mg^{2+} ion at the origin is at the center of the octahedron which shares two faces, and, because of the symmetrical sharing of these faces, the six Mg–F bond distances are the same, Table III. The F^-–F^- contacts forming the edges of this octahedron are also equal, and the F^-–Mg_2^{2+}–F^- angles deviate only ±8° from a right angle. (The crystallographically independent ions are labeled with subscripts, *e.g.*, Mg_1, Mg_2, F_1, F_2, F_3, etc., Table I.) The Mg_1^{2+} ion occupies the octahedron which shares one face and two corners. This octahedron is more irregular as can be seen from the Mg_1–F distances which vary from 1.89 to 2.10 Å, Table III. The long distances Mg_1–F_1 and Mg_1–F_3 are to F^- in the shared face, the shorter distances Mg_1–F_2 are to F^- ions which participate in corner sharing between two octahedra, and the shortest distance is to the F_4^- which is unshared. The F–Mg_1–F angles are also quite distorted with values ranging between 76.5 and 101°. The octahedron in α-Al_2O_3, where one octahedron shares one face, one edge, and one corner, shows similar irregularities.[8]

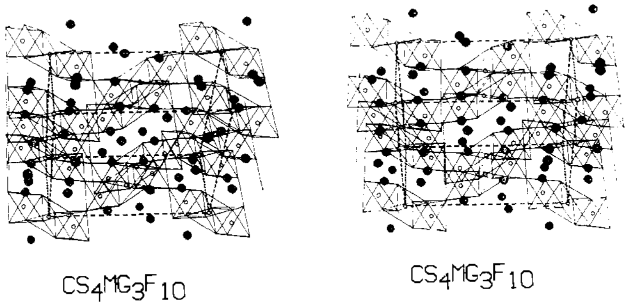

Figure 1.—A stereographic drawing of the linkages of octahedra in $Cs_4Mg_3F_{10}$. The unit cell is outlined by the dashed lines; the vertical axis is b and the horizontal axis is c. The structure is seen after a 50° rotation around the c axis.

The sum of the ionic radii for Cs^+ and F^- is 3.05 Å, and it is seen that the Cs^+–F^- distances vary from 3.05 to almost 3.5 Å. The environment around Cs_I is shown in Figure 2a. The 11 F^- ions form a nearly

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(5) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

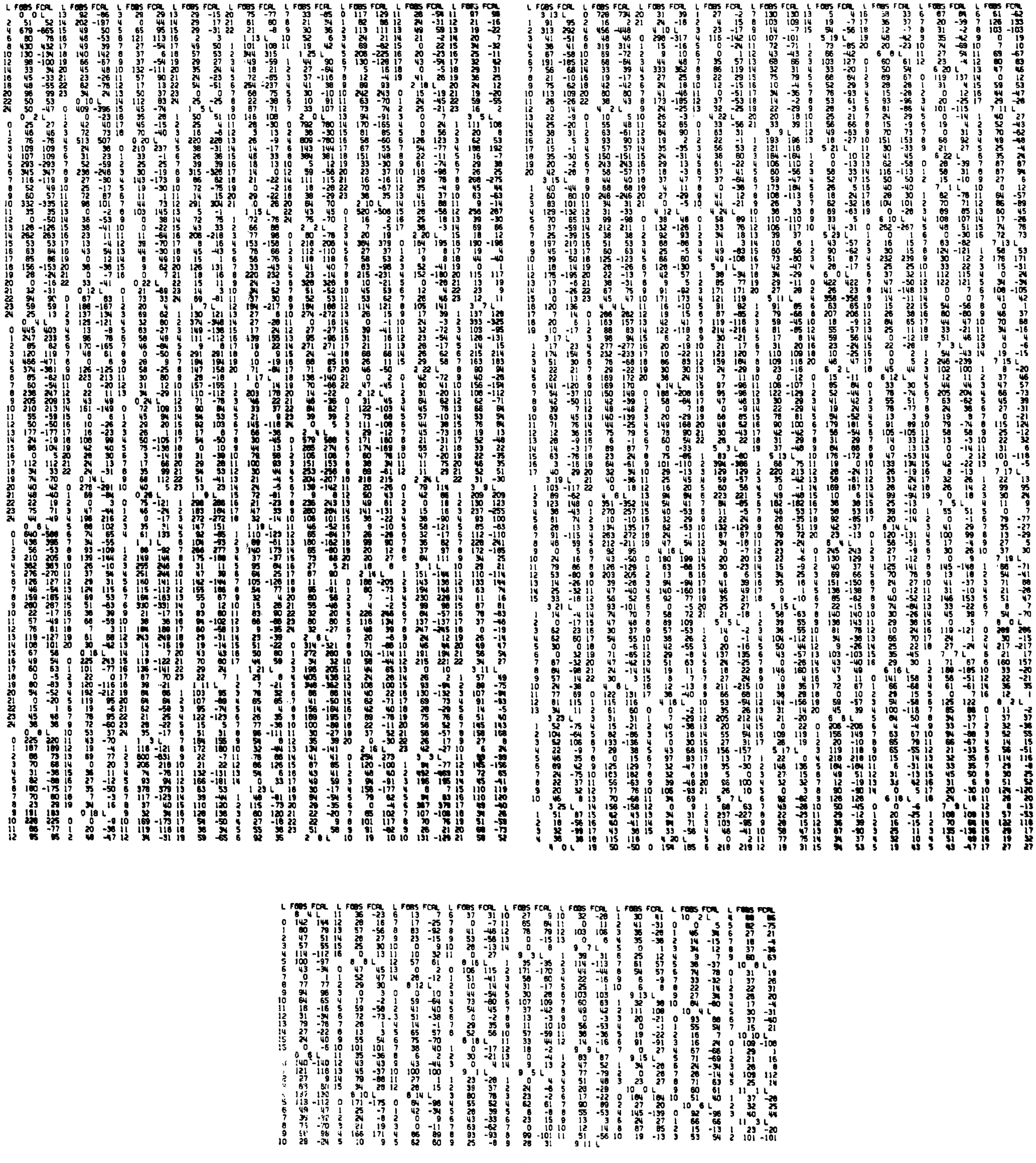
(6) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(7) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(8) R. E. Newnham and Y. M. De Haan, *Z. Krist.*, **117**, 235 (1962).

TABLE II[a]

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR $Cs_4Mg_3F_{10}$



[a] The signs of FCAL are the signs of the real part of the structure factor.

close-packed array with 2 F_1^-, F_4^-, 2 F_2^-, and F_4^- in the plane of Cs_1^+, 2 F_1^- and F_4^- above that plane, and F_3^- and F_4^- below the plane. The environment around Cs_2^+ consists of 10 anions, Figure 2b, and can be best described as consisting of a rectangular pyramid formed by 4 F_1^- forming the base and F_3^- at the apex with Cs_2^+ at the center; three anions, 2 F_3^- and F_4^-, project through three triangular faces of the pyramid and 2 F_2^- project through the centers of the edges of the fourth triangular face.

The F–F distances in the shared face are quite short, 2.575 and 2.606 Å, as expected. The two shortest Cs_1–F distances are to anions which are in the shared octahedral face while the short Cs_2–F distances are to the unshared anion and to one anion in a shared face.

The ellipsoids of thermal vibration, for most of the

TABLE III[a]

BOND DISTANCES AND ANGLES IN $Cs_4Mg_3F_{10}$

Distances, Å

Cs_1–F_1 (2)	3.048 (3)	Cs_2–F_3	3.007 (5)
Cs_1–F_4 (2)	3.122 (1)	Cs_2–F_3 (2)	3.089 (1)
Cs_1–F_3	3.228 (5)	Cs_2–F_1 (2)	3.092 (3)
Cs_1–F_1 (2)	3.229 (4)	Cs_2–F_1 (2)	3.098 (4)
Cs_1–F_2 (2)	3.261 (3)	Cs_2–F_2 (2)	3.192 (4)
Cs_1–F_4	3.357 (6)	F_1–F_1	2.575 (7)
Cs_1–F_4	3.471 (6)	F_1–F_3	2.606 (6)
Mg_1–F_4	1.890 (6)	F_1–F_2	2.881 (3)
Mg_1–F_2 (2)	1.989 (2)	F_1–F_4	2.940 (6)
Mg_1–F_1 (2)	2.077 (4)	F_1–F_3	2.982 (5)
Mg_1–F_3	2.104 (6)	F_1–F_1	2.999 (7)
Mg_2–F_1 (4)	1.977 (3)	F_2–F_4	2.872 (6)
Mg_2–F_3 (2)	1.984 (5)	F_2–F_3	2.909 (6)
Cs_2–F_4	2.940 (6)	F_2–F_2	3.067 (2)

Angles, Deg

F_4–Mg_1–F_2 (2)	95.9	F_2–Mg_1–F_1	163.7
F_4–Mg_1–F_1 (2)	95.2	F_1–Mg_2–F_1 (2)	97.8
F_2–Mg_1–F_2	101.0	F_1–Mg_2–F_1 (2)	82.2
F_2–Mg_1–F_1 (2)	89.8	F_1–Mg_2–F_3 (4)	97.8
F_2–Mg_1–F_3 (2)	90.9	F_1–Mg_2–F_3 (4)	82.2
F_1–Mg_1–F_1	77.3	F_3–Mg_2–F_3	180.0
F_1–Mg_1–F_3 (2)	76.5	F_1–Mg_2–F_1	180.0
F_4–Mg_1–F_3	169.2		

[a] The number in parentheses following the atom designations denotes the number of bonds with such a value around a cation. The number in parentheses following the distances is the standard deviation, $10^3\sigma$. Symmetry-equivalent atoms are not distinguished separately in the table.

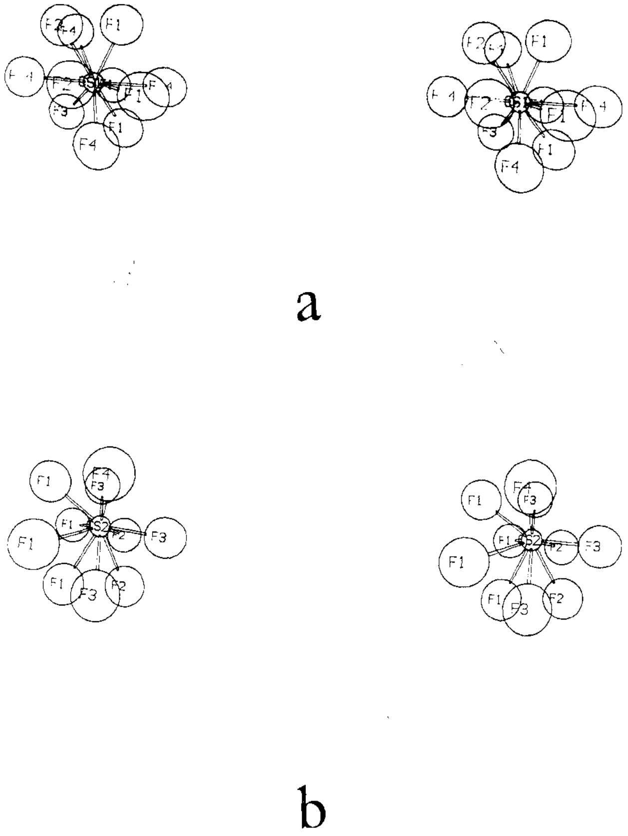


Figure 2.—(a) The coordination of F^- around Cs_1^+. (b) The coordination of F^- around Cs_2^+. The orientation is the same as in Figure 1.

TABLE IV

THE PRINCIPAL AXES, RMS THERMAL DISPLACEMENTS, AND ORIENTATIONS[a]

Atom	r	$\mu(r)$, Å	$c_{r,a}$	$c_{r,b}$	$c_{r,c}$
Cs_1	1	0.124 (1)	0	−0.966	−0.258
	2	0.128 (1)	−1	0	0
	3	0.164 (1)	0	0.258	−0.966
Cs_2	1	0.117 (1)	−1	0	0
	2	0.120 (1)	0	−0.438	−0.899
	3	0.129 (1)	0	−0.899	0.438
Mg_1	1	0.093 (5)	0	−1.000	−0.004
	2	0.104 (5)	−1	0	0
	3	0.106 (5)	0	0.004	−1.000
Mg_2	1	0.096 (7)	1	0	0
	2	0.102 (7)	0	0.752	0.659
	3	0.104 (7)	0	−0.659	0.752
F_1	1	0.096 (7)	0.882	0.133	−0.453
	2	0.129 (5)	−0.301	−0.581	−0.757
	3	0.151 (5)	0.363	−0.803	0.472
F_2	1	0.097 (9)	0.805	0	0.593
	2	0.141 (7)	0	1	0
	3	0.151 (7)	−0.593	0	0.805
F_3	1	0.111 (8)	0	−0.675	0.738
	2	0.139 (8)	0	0.738	0.675
	3	0.143 (8)	1	0	0
F_4	1	0.111 (9)	0	0.957	−0.288
	2	0.155 (9)	1	0	0
	3	0.195 (9)	0	0.288	0.957

[a] $\mu(r)$ is the rms displacement along axis r, and $c_{r,j}$ is the direction cosine between axis r and the jth cartesian axis.

atoms, are oriented with one of the principal axes along one of the crystallographic axes, Table IV. The Cs_2, Mg_1, and Mg_2 ions are vibrating isotropically, and since the latter two are confined to octahedral interstices, such isotropy can be expected. The Cs_1, F_2, F_3, and F_4 vibrations can be described by ellipsoids of revolution. The largest vibration direction of F_4 is perpendicular to the Mg_1–F_4 bond direction, which is physically realistic since this ion is not shared between octahedra.