JOURNAL OF SOLID STATE CHEMISTRY 64, 119–121 (1986)

BRIEF COMMUNICATION

The Crystal Structure of $Cs_{1-x}Lu_3F_{10-x}$: Refinement in a Higher Symmetry Space Group

RICHARD E. MARSH

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125*

Received November 22, 1985

The crystal structure of $Cs_{1-x}Lu_3F_{10-x}$, originally described in the monoclinic space group Cm, is better described in the hexagonal space group $P\bar{6}m2$. Least-squares refinement in $P\bar{6}m2$ has led to an improved R of 0.024, to more regular Lu–F distances, and to a revised composition parameter x of 0.10(1). © 1986 Academic Press, Inc.

The crystal structure of the nonstoichiometric compound $Cs_{1-x}Lu_3F_{10-x}$, $x \sim 0.25$, was recently described by Metin *et al.* (*1*). While preliminary diffraction photographs suggested the possible space groups $P6/mmm$, $P\bar{6}m2$, $P\bar{6}2m$, $P6mm$, or $P622$, the authors were unable to obtain satisfactory refinement in a hexagonal space group. Accordingly, they described the structure in the monoclinic space group Cm (a = 13.764(5), b = 7.947(1), c = 4.229(2) Å, β = 90.04(5)°, Z = 2) and obtained refinement to an R of 0.053 for 2038 independent reflections. Since, as Metin *et al.* note (*1*), the derived structure departs only slightly from hexagonal symmetry, I have pursued the matter further and have derived a more satisfactory structure in space group $P\bar{6}m2$.

The hexagonal unit cell, derived from the vectors $\frac{1}{2}(\mathbf{a} - \mathbf{b})$, $\mathbf{b}$, $\mathbf{c}$, has dimensions a_h = 7.943, c_h = 4.227 Å, Z = 1 (*1*). A listing of observed F's was kindly provided by Dr. J. C. Cousseins; it contains 1974 reflections in the quadrant $-27 \le h \le 27$, $0 \le k \le 15$, $0 \le l \le 8$ (monoclinic indexes). After transforming to hexagonal indexes and averaging according to Laue symmetry $6/mmm$, 398 independent reflections resulted. The agreement among the various equivalent forms (up to six) was very good, the discrepancies $|F - \hat{F}|$ between an individual measurement and the averaged value averaging to about 3% of $\hat{F}$. Thus, the hexagonal symmetry is confirmed. One reflection—$\bar{1}8,6,2$ in the monoclinic indexing—was omitted from the averaging, since its F_0 value of 43.1 was in severe disagreement both with the other two equivalent hexagonal forms (111.7 and 112.6) and with the F(cal) value for the monoclinic structure (110.4).

The starting model in $P\bar{6}m2$ was obtained by transforming the Cm coordinates (Ref. (*1*), Table III) and averaging over equivalent atoms. Full-matrix least-squares refinement then converged at an R of 0.024 for

* Contribution No. 7329.

0022-4596/86 $3.00

TABLE I

FINAL PARAMETERS, SPACE GROUP $P\bar{6}m2$

Atom	x	y	z	U_{11}	U_{33}	U_{12}
Lu(1,2)	0.49136(6)	$-x$	0	0.0079(1)	0.0064(1)	0.0038(2)
Cs	0	0	$\frac{1}{2}$	0.0367(17)	0.0220(8)	$\frac{1}{2}U_{11}$
F(1,3)	−0.2172(18)	$-x$	0	0.011(2)	0.053(8)	−0.003(3)
F(2,4)	0.1650(21)	$-x$	0	0.014(3)	0.048(8)	0.007(4)
F(5)	$\frac{1}{3}$	$\frac{2}{3}$	0.119(7)	0.006(4)	0.034(13)	$\frac{1}{2}U_{11}$
F(6,7)	0.5139(20)	$-x$	$\frac{1}{2}$	0.012(6)	0.008(2)	−0.003(3)

Note. The form for the U's is $\exp(-2\pi^2)(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)$. $U_{22} = U_{11}$ and $U_{13} = U_{23} = 0$ for all atoms.

398 reflections and 25 parameters (including an extinction parameter; final value, 5.7(2) $\times 10^{-6}$). The $P\bar{6}m2$ parameters are given in Table I.

While the $P\bar{6}m2$ structure is similar to the *Cm* structure described earlier (*1*), there are some significant differences:

(1) F(5) rather than F(6) occupies a partially-occupied site.

(2) The occupancy factor for the Cs site is 0.90(1) rather than 0.75(1), and that for F(5) is 0.50(5) rather than 0.75(8) for F(6). The composition of the compound (assuming all other sites to be fully occupied) thus becomes $Cs_{0.90(1)}Lu_3F_{10.0(1)}$—or, presumably, $Cs_{0.9}Lu_3F_{9.9}$.

(3) The range of Lu–F distances in the (approximate) pentagonal bipyramid is appreciably reduced, from 2.02(7)–2.26(2) Å in the *Cm* description to 2.13(3)–2.25(3) Å. The Cs–F distances remain irregular, with six Cs–F(2,4) at 3.10(3), six Cs–F(1,3) at 3.66(3), and three Cs–F(6,7) at 3.98(3) Å. The Cs atom lies at a site of $P\bar{6}m2$ symmetry.

Metin *et al.* (*1*) point out that, for their *Cm* model, "the departure from the hexagonal symmetry is practically exclusively due to the F(5) fluorine atom which deviates from the (001) plane". In the $P\bar{6}m2$ description, this atom is disordered between two sites, 1.02 Å apart, on opposite sides of the mirror plane at $z = 0$. Removing this mirror plane so as to create an ordered structure would reduce the Laue symmetry to $\bar{3}m$ (space group *P3m*). There is no evidence of the lower Laue symmetry: averaging the F_0 value in $\bar{3}m$ results in essentially the same agreement (3%) as obtained in 6/*mmm*. Nor was there any improvement in averaging according to $\bar{6}m2$ symmetry, indicating that anomalous dispersion effects are undetectably small for this nearly centrosymmetric structure. Deviations from the centrosymmetric space group *P6/mmm* are no larger than 0.3 Å; however, refinement of the *P6/mmm* model was unsuccessful, R remaining at about 0.23.

Note. The structure of the related compound $CsYb_3F_{10}$, originally described in the monoclinic space group *Pc* (*2*), has also been revised and re-refined in the orthorhombic space group *Pmcm* (*3*). In addition, the structure of $RbIn_3F_{10}$, described in the noncentrosymmetric orthorhombic space group $P222_1$ (*4*), should probably be described in the centrosymmetric *Pmcm*. I have not attempted to obtain a listing of F_0's for this latter compound.

Acknowledgments

I am indebted to J. C. Cousseins for a listing of F values and for his encouragement, to B. J. Westphal

and K. M. Slagle for computing assistance, and to the National Institutes of Health for financial support (Grant GMS 16966).

References

1. J. METIN, D. CHATONIER, D. AVIGNANT, R. CHEVALIER, AND J. C. COUSSEINS, *J. Solid State Chem.* **55,** 299 (1984).
2. S. ALEONARD, M. TH. ROUX, AND B. LAMBERT, *J. Solid State Chem.* **42,** 80 (1982).
3. R. E. MARSH, *J. Solid State Chem.* **47,** 242 (1983).
4. J. C. CHAMPANAUD-MESJARD, D. MERCURIO, AND B. FRIT, *J. Inorg. Nucl. Chem.* **39,** 947 (1977).