

Anion and Cation Defect Structure in Magnesium Fluorogermanate

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Single crystals of magnesium fluorogermanate have been grown from a melt composition of $3.5\text{MgO}\cdot 0.5\text{MgF}_2\cdot \text{GeO}_2$ in a lead fluoride flux. The crystals are isomorphous with magnesium germanate, $\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}$; the space group is *Pbam* and $a = 14.343(1)$, $b = 10.196(1)$, and $c = 5.9075(4)$ Å. A final unit cell composition of $\text{Mg}_{28}\text{Ge}_{7.5}\text{O}_{38}\text{F}_{10}$ was deduced from a detailed analysis of high quality X-ray diffraction data. A residual, $R = 0.045$, was achieved with a data-parameter ratio of 17 in the final anisotropic refinement.

Analysis of scattering factors, thermal parameters and site occupancy factors revealed defect clusters centered around a partial germanium vacancy (38.8% occupied) at a unique tetrahedral site. Fluorine and oxygen occupancies of the contiguous anion sites are discussed in detail.

Introduction

It has recently been shown (1) in a very precise X-ray diffraction analysis, that the compound known as magnesium germanate has a novel crystal structure with a unit cell composition $\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}$. When activated with less than 1% of quadrivalent manganese, this compound is a phosphor with strong emission in the red region of the optical spectrum. It is well known (2) that partial substitution of magnesium fluoride for magnesium oxide in the preparation of this phosphor greatly improves its fluorescence characteristics. (The origin of this enhancement is unknown, but it is clear that some fluorine is incorporated into the compound with appropriate charge compensation from a change in cation composition.) It has been possible to prepare a single crystal of such a magnesium fluorogermanate, and we provide herein a detailed description of the disposition of fluorine atoms in anion clusters around partially vacant germanium sites.

Experimental

Preparation and Analysis

Magnesium fluorogermanate was prepared by the same method used (1) to prepare magnesium germanate excepting that magnesium fluoride was added to the preparation. Magnesium oxide (Mallinckrodt Analytical Reagent), magnesium fluoride (Crystal Grade, Sylvania Electric Products,

Inc.), germanium dioxide (Electronic Grade, Kawecki Chemical Co.) in a mole ratio of 3.5:0.5:1.0, with 1 mole% of manganese carbonate (Fisher Certified Reagent) added as a fluorescence activator, were mixed and ground in acetone. After removal of acetone at 110°C, the mixture was fired in air in a covered platinum crucible at 1100°C for 1 hr; it was then reground and fired for 16 hr at 1200°C.

Single crystals of magnesium germanate were grown (1) from a lead oxide flux. In the present case, in order to maximize the incorporation of fluorine into the compound and to help establish an equilibrated final composition, a lead fluoride flux was used. A mixture of 67.5 g of lead fluoride (Extra Pure Grade, BDH Chemicals Co., Ltd.) and 6.75 g of magnesium fluorogermanate in a 50 ml tightly covered platinum crucible was heated in dry oxygen at 1250°C for 4 hr. The silicon carbide resistance furnace was cooled at about 4°/hr to 900°C and the product was then removed. The crystals were separated mechanically and the remaining flux was dissolved in hot water; this solubility is a distinct advantage of the lead fluoride flux.

A semiquantitative emission spectrographic analysis (3) of single crystals revealed the following approximate weight percents of impurities: manganese (0.1–1.0%), platinum (0.01–0.10%), lead (0.01–0.10%), silicon (0.01–0.10%), copper (0.001–0.01%), aluminum (0.001–0.01%). This is essentially the same impurity composition found (1) for the magnesium germanate crystals.

A composite analysis (3) of the crystals was undertaken in which magnesium was determined after dissolution by atomic absorption, germanium by calibrated neutron activation analysis and fluorine by potentiometric titration. The results, in weight percent, are compared with calculated values based upon the composition $\text{Mg}_{28}\text{Ge}_{7.5}\text{O}_{38}\text{F}_{10}$:

	Calculated	Found
Mg	33.6	$33.3 \pm 1.0\%$
Ge	26.9	$27.0 \pm 1.5\%$
F	9.4	$8.1 \pm 0.9\%$

It is clear from these results that fluorine was incorporated into the crystal structure and that charge compensation was achieved by deficiencies in germanium content relative to the magnesium germanate composition, $\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}$.

X-Ray Diffraction

The crystals were generally tabular in form and many exhibited numerous small inclusions of flux. Specimens were frequently macroscopically twinned on a plane later identified as (031). A suitable individual was carefully ground to a sphere of diameter 0.018 ± 0.001 cm; Weissenberg and precession photographs revealed orthorhombic symmetry with systematic absences corresponding to the space groups $Pb\bar{m}$ or $Pb2_1$.

Lattice constants were determined from a least-squares analysis of 48 independent reflections that were automatically centered on a Picker FACS-1 four-circle diffractometer with $\text{MoK}\alpha_1$ radiation. The data, spanning the angular range $40^\circ < 2\theta < 65^\circ$, yielded the parameters $a = 14.342(1)$, $b = 10.196(1)$, $c = 5.9075(4)$ Å. The calculated density, based upon the composition $\text{Mg}_{28}\text{Ge}_{7.5}\text{O}_{38}\text{F}_{10}$, is 3.89 g/cm³ and the observed density was $3.87(1)$ g/cm³.

Diffraction intensities were measured with Zr-filtered $\text{MoK}\alpha$ radiation at a takeoff angle of 2.5° . The diffractometer was operated in a θ - 2θ scan mode with a scan rate of one degree 2θ per minute over a range of 1.5° ; the scan range was continuously adjusted for dispersion and 40 sec background counts were taken at both ends of the scan. Of the 2308 independent intensities accessible in the angular range $2\theta \leq 71^\circ$, a total of 2080 were observable according to the criterion $|F_o| > 0.670\sigma_F$, wherein $\sigma_F = 0.02|F_o| + [C + k^2 B]^{1/2}/2|F_o|L_p$; the total scan count is C , and k is the ratio of scanning time to the total background count B . Three reflections were systematically monitored and no random variations in intensity greater than 3.5% were observed over the entire data collection period; the mean variation was very much smaller.

The intensity data were corrected for Lorentz and polarization effects and absorption corrections (4) were applied for a spherical crystal with $\mu R = 0.84$; the maximum absorption correction applied was 4% of $|F_o|$. Isotropic extinction corrections (5) were also applied in the least-squares refinement stage of the structure analysis. In the final refinement, the maximum extinction correction was 23.5% of $|F_c|$ for the 004 reflexion.

Analysis of the Structure

It was clear from the lattice constants, the space group and the general intensity distribution that the structure was isomorphous with magnesium germanate (I), $\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}$. This was confirmed with a Patterson synthesis in which the major difference between the structures appeared in the magnitude of the Ge III-Ge III (I) interaction peak. Nevertheless, a structure model based upon the magnesium germanate parameters yielded a conventional residual, R , of only 0.36 with isotropic temperature factors for all atoms. A variable occupancy parameter for the Ge III site reduced the R value to 0.052 in two cycles. When, in a subsequent cycle, the occupancy factors of all atoms in the structure were allowed to vary, R dropped only slightly to 0.050. The occupancy of the Ge III site remained near 38% but all oxygen sites coordinated to this germanium showed extra electron density corresponding to oxygen occupancy of 107-115%. The occupancy factors of all other oxygen, germanium, and magnesium atom sites remained close to unity.

From these results on the germanate model, it was evident that the principal factor in the minimization of the statistical residual was a major vacancy concentration at the Ge III site. The analysis was considerably less sensitive to changes at the anion sites but, fortunately, data were available in sufficient quantity and quality to warrant a detailed statistical comparison of alternative structural models. The results for five cases are presented in Table I; the values for the residuals, percent occupancies and thermal parameters are taken from the third cycle of full-matrix least-squares refinement for each model. Occupancy factors were varied only for the atom sites that were labeled Ge III, O IV, O VI and O IX in the germanate structure (I); these cation and anion sites are labeled C III, A IV, A VI and A IX, respectively. The coordinates and thermal parameters of all other atoms were also refined, but they were essentially identical in all of the analyses. Atomic scattering factors for Mg^+ and $\text{F}^{-0.5}$ were interpolated from tables (6) and standard tabulated

TABLE I

Model	Cation	Anions	R_1, R_2	% Occupancy				Isotropic Thermal Parameters (B) Å ²			
				C III	A IV	A VI	A IX	C III	A IV	A VI	A IX
I	Mg ¹⁺	O ⁻¹	0.0503 0.0769	112(1)	107(1)	115(2)	113(1)	-0.21(2)	0.25(5)	1.18(7)	0.79(4)
II	Mg ¹⁺	F ^{-0.5}	0.0500 0.0764	113(1)	89(1)	97(1)	95(1)	-0.20(2)	0.22(5)	1.18(7)	0.77(4)
III	Ge ²⁺	O ⁻¹	0.0500 0.0763	38.6(2)	107(1)	115(2)	113(1)	0.26(2)	0.26(5)	1.19(7)	0.77(4)
IV	Ge ²⁺	F ^{-0.5}	0.0497 0.0760	38.8(2)	89(1)	97(1)	95(1)	0.26(2)	0.23(5)	1.20(7)	0.74(4)
V	Ge ²⁺	F ^{-0.5}	0.0453 0.0698	38.8(2)	89(1)	97(1)	95(1)	0.26(2) ^a	0.20(5) ^a	0.96(7) ^a	0.62(4) ^a

^a Anisotropic thermal parameters were used for all atoms. The values of B recorded here are derived from these in an averaging procedure.

(6, 7) forms were used for Ge²⁺ and O⁻; anomalous scattering terms (8) were also included for germanium.

Models I and II contain magnesium as the cation in the C III site, in one case with oxygen neighbors and, in the other, with fluorine. After refinement, the cation occupancy factors were 112% and 113% and the associated thermal parameters were negative. These results clearly demonstrate that magnesium cannot provide the electron density required at the cation site. On the other hand, with germanium as the cation in Models III and IV, the occupancy of site C III dropped to 38.8% with a slight but statistically significant decrease in the residuals as compared to the corresponding Models I and II. Moreover, the cation thermal parameters ($B = 0.26$ Å²) were positive and nearly isotropic, and were smaller than the Ge III parameter ($B = 0.39$ Å²) found in the germanate structure. Finally, the anion occupancy factors and thermal parameters were essentially unaffected by the interchange of magnesium and germanium at site C III.

These observations strongly support the view that no magnesium substitution occurs at C III and that the site is partially occupied by 38.8% germanium. Even with germanium, the thermal parameters at the site are remarkably low and remarkably isotropic for a defect structure; with a mixed cation occupancy, the thermal parameter would become improbably low. Finally, considering the attendant changes in the adjacent anion sites, it is unlikely that two different cations would take positions that superpose identically to give a spherically symmetric electron density distribution.

Model IV was subjected to a further refinement with anisotropic thermal parameters for all atoms. The results are recorded as Model V in Table I and in complete detail in Table II. The decrease in the weighted R value, although small, was significant at the 99.5% confidence level on the basis of Hamilton's statistical R -ratio test (9). The isotropic analysis included more than 35 independent data for each of the 59 parameters; the data-parameter ratio was 17 in the anisotropic refinement.¹ The over-all quality of the analysis fully equalled that of the original germanate structure.

None of the coordinates or occupancy factors was changed significantly by the anisotropic refinement. The resulting thermal parameters were essentially isotropic with average values close to those found in the parent germanate structure; the fluorine atoms in sites A VI and A IX were exceptional in that the parameters were substantially larger and markedly anisotropic (Table II). At each of these two sites, the long axis of the thermal ellipsoids is directed away from the tetrahedral site Ge III and toward the center of a contiguous empty site with octahedral coordination. A perspective view of the site geometry and anisotropy around Ge III is shown in Fig. 1.

¹ A table of $|F_0|$ and $|F_c|$ has been deposited as Document No. NAPS-01555 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, NY 10022. A copy may be secured by citing the document number and by remitting \$5.00 for photocopies of \$2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

TABLE II
FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS^{a,b}

Atom	Point symmetry	10 ⁴ x	10 ⁴ y	10 ⁴ z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ge I	2/m	0	0	0	0.24(2)	0.21(2)	0.21(2)	-0.00(1)	0	0
Ge II	m	1254(1)	5006(1)	0	0.20(2)	0.20(2)	0.22(2)	0.01(1)	0	0
Ge III	m	1860(1)	3266(1)	½	0.18(4)	0.30(4)	0.32(4)	-0.05(3)	0	0
Mg I	2/m	0	½	½	0.70(8)	0.28(7)	0.21(7)	-0.10(5)	0	0
Mg II	2/m	0	0	½	0.41(7)	0.33(7)	0.18(7)	0.05(5)	0	0
Mg III	m	1751(1)	1777(1)	0	0.28(5)	0.36(5)	0.35(5)	-0.00(4)	0	0
Mg IV	m	3230(1)	1521(1)	½	0.60(5)	0.43(5)	0.44(5)	-0.13(4)	0	0
Mg V	1	-36(1)	2524(1)	2428(1)	0.48(3)	0.29(3)	0.27(3)	-0.05(3)	0.02(3)	-0.00(3)
Mg VI	1	3297(1)	4176(1)	2477(1)	0.30(3)	0.35(3)	0.26(4)	0.03(3)	-0.01(3)	0.06(3)
O I	m	843(2)	3363(2)	0	0.30(9)	0.19(9)	0.42(9)	-0.14(7)	0	0
O II	m	4220(2)	3491(2)	0	0.09(8)	0.27(9)	0.49(10)	-0.14(7)	0	0
O III	m	2502(2)	24(2)	0	0.57(10)	0.45(10)	0.35(10)	-0.05(7)	0	0
F IV	m	651(1)	3309(2)	½	0.22(10)	0.22(9)	0.18(9)	0.00(7)	0	0
O V	m	4119(2)	3303(3)	½	0.40(10)	0.38(9)	0.14(9)	0.08(7)	0	0
F VI	m	2467(2)	-87(3)	½	1.88(15)	1.42(14)	0.51(11)	-0.97(10)	0	0
O VII	1	762(1)	778(1)	2241(3)	0.24(6)	0.27(6)	0.25(6)	0.04(5)	-0.03(5)	-0.08(5)
O VIII	1	4136(1)	809(2)	2499(3)	0.34(7)	0.33(6)	0.35(7)	0.01(5)	-0.01(5)	-0.01(5)
F IX	1	2497(1)	2509(1)	2586(3)	1.27(9)	0.44(7)	0.56(8)	-0.09(6)	-0.42(6)	-0.02(5)

^a Numbers in parentheses are estimated standard deviations in last significant figure.

^b Coordinates of 0 or ½ are determined by site and space group symmetry.

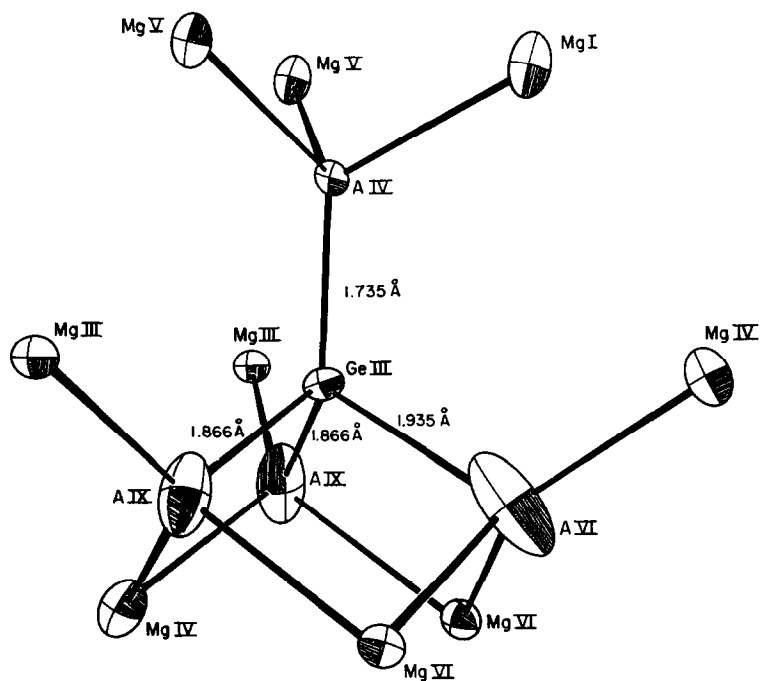


FIG. 1. The cation-anion defect cluster centered around the cation site Ge III in magnesium fluorogermanate. Thermal ellipsoids are shown in perspective.

TABLE III

REFINED PARAMETERS FOR HALF-ATOMS AT SITES A VI AND A IX; RESIDUAL $R = 0.046$ and $R_w = 0.072$

Atom	$10^4 x$	$10^4 y$	$10^4 z$	$B (\text{\AA}^2)$	Occupancy
F ₁ VI	2541(14)	-176(17)	$\frac{1}{2}$	0.30(22)	0.48(8)
F ₂ VI	2385(15)	11(18)	$\frac{1}{2}$	0.85(17)	0.48(8)
F ₁ IX	2346(22)	2518(7)	2681(36)	0.37(21)	0.48(16)
F ₂ IX	2560(21)	2501(6)	2488(32)	0.53(14)	0.48(16)

An alternative description of anisotropic thermal motion involves a two-state model in which the anisotropy results from the apparent superposition of two fractionally weighted atoms displaced on either side of the center along the major axis of the ellipsoid. Such a model is an attractive possibility for sites A VI and A IX because of the partial occupancy of the coordinated Ge III site; it is clear that such a displacement could be coupled with the

presence or absence of a germanium atom at that site.

Two fluorine atoms were placed at each of the sites A VI and A IX with occupancy factors set at one-half of the values found in Model IV. These atoms were assigned thermal parameters corresponding to the minor axes of their respective anisotropic thermal ellipsoids and all other atoms were given isotropic thermal parameters from Model IV. A least-squares refinement of the positional parameters for these four half-atoms quickly converged and yielded final residuals, $R = 0.046$ and $R_w = 0.072$. These values are very close to the final values achieved with the full anisotropic refinement of Model V. This clearly demonstrates that the anisotropy at these two sites is the only structurally significant feature imbedded in the anisotropic thermal analysis.

The two half-atoms are labeled F₁ and F₂ at each of the anion sites, A VI and A IX. At each of the sites, the two-state model refinement placed one of

TABLE IV

BOND DISTANCES, POLYHEDRAL EDGE LENGTHS, AND BOND ANGLES FOR GERMANIUM ATOMIC POSITIONS^a

Atoms	Distance (Å)	Atoms	Angle (degrees)
Ge I-O II	1.901(3)	O II-Ge I-O VII	89.9(1)
Ge I-O VII	1.896(2)	O II-Ge I-O VII	90.0(1)
O II-O VII	2.684(3)	O VII-Ge I-O VII	89.1(1)
O II-O VII	2.686(3)	O VII-Ge I-O VII	90.8(1)
O VII-O VII	2.662(4)	O VII-Ge I-O VII	180.0
O VII-O VII	2.702(4)		
Ge II-O I	1.775(3)	O I-Ge II-O III	109.9(1)
Ge II-O III	1.782(4)	O I-Ge II-O VIII	109.2(1)
Ge II-O VIII	1.785(2)	O III-Ge II-O VIII	107.9(1)
O I-O III	2.914(5)	O VIII-Ge II-O VIII	112.4(1)
O I-O VIII	2.985(3)		
O III-O VIII	2.886(4)		
O VIII-O VIII	2.968(4)		
Ge III-F IV	1.734(3) ^b	F IV-Ge III-F VI	118.4(2)
Ge III-F VI	1.935(4)	F IV-Ge III-F IX	120.0(1)
Ge III-F IX	1.866(2)	F VI-Ge III-F IX	96.5(1)
F IV-F VI	3.154(5)	F IX-Ge III-F IX	100.2(1)
F IV-F IX	3.119(3)		
F VI-F IX	2.838(4)		
F IX-F IX	2.865(5)		

^a Numbers in parentheses are estimated standard deviations in last significant figure.

^b "Axial" bond.

the half-atoms, F_1 , precisely at the same position occupied by the oxygen anion in the germanate structure, with almost exactly the same thermal parameter. The other half-atoms of fluorine, F_2 VI and F_2 IX, were located 0.28 Å and 0.18 Å further away from the Ge III site, respectively.

A further probe of the two-state model was undertaken by allowing the thermal parameters and occupancy factors for the four half-atoms to vary along with the atom coordinates in three cycles of least-squares analysis; the results are listed in

Table III. The coordinates were unchanged but the correlation matrices indicated considerable interdependency among the other parameters. The resulting standard deviations are large, but it does appear that the thermal parameters for the F_1 VI and F_1 IX sites ($B \approx 0.3 \text{ \AA}^2$) are the same found for other anions in the structure while those for F_2 VI and F_2 IX are much larger ($B = 0.85$ and 0.53 \AA^2 , respectively). The total occupancies of A VI and A IX drop slightly to 96% in this refinement, but only by one or two standard deviations.

TABLE V
BOND DISTANCES AND POLYHEDRAL EDGE LENGTHS FOR THE MAGNESIUM
ATOMIC POSITIONS^a

Atoms	Distance (Å)	Atoms	Distance (Å)
Mg I-F IV	1.960(3)	Mg II-O V	2.141(3)
Mg I-O VIII	2.102(2)	Mg II-O VII	2.123(2)
F IV-O VIII	2.780(3)	O V-O VII	3.012(3)
F IV-O VII	2.965(3)	O V-O VII	3.018(3)
O VIII-O VIII	2.968(4)	O VII-O VII	2.662(4)
O VIII-O VIII	2.978(4)	O VII-O VII	2.702(4)
Mg III-O I	2.075(3)	Mg IV-O V	2.220(4)
Mg III-O III	2.087(4)	Mg IV-F VI	1.971(4)
Mg III-O VII	2.195(2)	Mg IV-O VIII	2.102(2)
Mg III-F IX	2.015(2)	Mg IV-F IX	2.042(2)
O I-O VII	2.954(3)	O V-O VIII	2.945(3)
O I-F IX	2.956(3)	O V-F IX	2.849(3)
O III-O VII	2.931(4)	F VI-O VIII	2.960(4)
O III-F IX	2.989(3)	F VI-F IX	2.838(4)
O VII-O VII	2.702(4)	O VIII-O VIII	2.968(4)
O VII-F IX	3.057(3)	O VIII-F IX	2.920(3)
F IX-F IX	2.865(5)	F IX-F IX	2.865(5)
Mg V-O I	2.098(3)	Mg VI-O II	2.098(2)
Mg V-O II	2.070(3)	Mg VI-O III	2.056(3)
Mg V-F IV	1.986(2)	Mg VI-O V	2.103(2)
Mg V-O V	2.124(2)	Mg VI-F VI	2.002(3)
Mg V-O VII	2.119(2)	Mg VI-O VII	2.122(2)
Mg V-O VIII	2.072(2)	Mg VI-F IX	2.052(2)
O I-O II	2.999(4)	O II-O III	2.924(5)
O I-F IV	2.9821(5)	O II-O V	2.9784(4)
O I-O VII	2.954(3)	O II-O VII	2.684(3)
O I-O VIII	2.985(3)	O II-F IX	3.077(3)
O II-O V	2.9784(4)	O III-F VI	2.9714(3)
O II-O VII	2.686(3)	O III-O VII	2.931(4)
O II-O VIII	3.113(3)	O III-F IX	2.989(3)
F IV-O V	2.745(4)	O V-F VI	2.804(5)
F IV-O VII	3.060(3)	O V-O VII	3.012(3)
F IV-O VIII	2.780(3)	O V-F IX	2.849(3)
O V-O VII	3.012(3)	F VI-O VII	3.073(4)
O V-O VIII	2.945(3)	F VI-F IX	2.838(4)

^a Numbers in parentheses are estimated standard deviations in the last significant figure.

The possible structural implications of these striking results are obvious. The occupancy factors in Table I make it clear that oxygen atoms cannot supply the necessary electron density at any of the anion sites in question, whereas a deficiency of fluorine is required in Models II, IV, and V. Complete occupancy of the anion sites could be assured by considering a mixture of fluorine and oxygen at each site. Since a germanium atom occupies the Ge III site only 3/8 of the time, it is possible that each germanium is associated with an oxygen atom at A₁ VI, A₁ IX and A IV; fluorine could then be associated with the germanium vacancy.

A careful analysis was undertaken of the contributions to the electron densities at the anion sites by weighting the atomic scattering factors for fluorine and oxygen with the observed occupancy factors and thermal parameters. The comparisons were made as a function of the distribution with respect to $\sin\theta/\lambda$ of the observed structure amplitudes. The analysis was complicated by the fact that the scattering curves for the two atoms, scaled by occupancy and thermal factors, crossed in each case at a value of $\sin\theta/\lambda$ near the peak in the data distribution curve. Nevertheless, the best estimate for a mixed occupancy model resulted in the following site compositions:

	Fluorine	Oxygen
A IV	0.33(5)	0.67(5)
A VI	0.81(5)	0.19(5)
A IX	0.69(5)	0.31(5)

These results do not support the simplified version of a mixed occupancy model in which germanium vacancies are directly associated with four fluorine neighbors, but they do indicate that plausible models involving both anions could be developed. Of greater importance is the fact that the average fluorine substitution corresponding to these results is 63% of the sites coordinated to Ge III. With 61.2% germanium vacancies, it is evident that within experimental error, the model provides over-all charge balance in the structure. Moreover, the over-all composition calculated from the model is $\text{Mg}_{28}\text{Ge}_{7.5}\text{O}_{38}\text{F}_{10}$ which, as indicated above, is in good agreement with the experimental analytical results.

As attractive as the mixed occupancy model is, particularly when combined with the features of the two-state model for sites A VI and A IX, it is not appropriate to extend it further without some additional experimental check on its validity. An interesting possibility involves the observation that

TABLE VI
SELECTED BOND ANGLES (DEGREES) FOR
THE MAGNESIUM ATOMIC POSITIONS^a

Atom	(O-M-O) _{max}	(O-M-O) _{min}
Mg I	93.7(1)	86.3(1)
Mg II	100.9(1)	79.0(1)
Mg III	99.3(1)	74.6(1)
Mg IV	97.1(1)	83.7(1)
Mg V	97.4(1)	83.7(1)
Mg VI	95.6(1)	78.9(1)

^a Numbers in parentheses are estimated standard deviations in last significant figure.

on very long exposures, extremely weak reflexions appear that indicate that the glide planes are violated in the fluorogermanate. The phenomenon has been observed by electron diffraction and the possibility of lamellar intergrowth structures is being studied.

For purposes of comparison with the parent germanate structure, all of the relevant structural data based upon Model V are presented in Tables IV-VI. For convenience, fluorine occupancy is assumed at A IV, A VI and A IX in all of the listings.

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