

- (34) D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1013 (1974).
- (35) C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).
- (36) L. S. Childers, K. Foltz, L. L. Merritt, Jr., and W. E. Streib, *Acta Crystallogr., Sect. B*, **31**, 924 (1975).
- (37) Calculated from the data in ref 36.
- (38) D. K. Johnson, H. J. Stoklosa, J. R. Wasson, and H. E. Montgomery, *J. Inorg. Nucl. Chem.*, **36**, 525 (1974).
- (39) J. R. Wasson, H. W. Richardson, and W. E. Hatfield, *Z. Naturforsch. B*, **32**, 551 (1977).
- (40) S. N. Choi, R. D. Bereman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).
- (41) J. R. Wasson, D. M. Klassen, H. W. Richardson, J. W. Hall, and W. E. Hatfield, submitted for publication.
- (42) D. W. Smith, *Coord. Chem. Rev.*, **21**, 93 (1976).
- (43) A. B. P. Lever, *J. Chem. Educ.*, **51**, 612 (1974).
- (44) B. D. Bird and P. Day, *J. Chem. Phys.*, **49**, 392 (1968); J. C. Rivoal and B. Briat, *Mol. Phys.*, **27**, 1081 (1974).
- (45) J. Demuyneck, A. Veillard, and U. Wahlgren, *J. Am. Chem. Soc.*, **95**, 5563 (1973).
- (46) E. W. Wilson, Jr., M. H. Kasperian, and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 5365 (1970).
- (47) R. A. Vaughan, *Phys. Status Solidi B*, **49**, 274 (1972).
- (48) G. F. Kokoszka, C. W. Reimann, and H. C. Allen, *J. Phys. Chem.*, **71**, 121 (1967).
- (49) J. R. Wasson, *Spectrosc. Lett.*, **9**, 95 (1976).
- (50) J. A. Fee, *Struct. Bonding (Berlin)*, **23**, 1 (1975).
- (51) E. I. Solomon, J. W. Hare, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1389 (1976).
- (52) O. Siiman, N. M. Young, and P. R. Carey, *J. Am. Chem. Soc.*, **98**, 744 (1976).
- (53) H. Yokoi and A. W. Addison, *Inorg. Chem.*, **16**, 1341 (1977); U. Sakaguchi and A. W. Addison, *J. Am. Chem. Soc.*, **99**, 5189 (1977).
- (54) A. J. Freeman and R. E. Watson, "Magnetism", Vol. IIA, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N.Y., 1965, p 67.
- (55) M. Sharnoff, *J. Chem. Phys.*, **42**, 3383 (1963); C. A. Bates, W. S. Moore, K. J. Standley and K. W. H. Stevens, *Proc. Phys. Soc., London*, **79**, 73 (1963).
- (56) H. Yokoi, *Bull. Chem. Soc. Jpn.*, **47**, 3037 (1974).

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Departments of Chemistry and Physics, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

## A Neutron Diffraction Investigation of the Crystal and Molecular Structure of the Anisotropic Superconductor $\text{Hg}_3\text{AsF}_6$

ARTHUR J. SCHULTZ,<sup>1a</sup> JACK M. WILLIAMS,<sup>\*1a</sup> NEMESIO D. MIRO,<sup>1b</sup> ALAN G. MACDIARMID,<sup>\*1b</sup> and ALAN J. HEEGER<sup>\*1c</sup>

Received July 7, 1977

The crystal and molecular structure of  $\text{Hg}_3\text{AsF}_6$  has been investigated by single-crystal neutron diffraction. This metallic compound crystallizes in the body-centered tetragonal space group  $I4_1/amd$  with cell dimensions of  $a = 7.549$  (5) Å and  $c = 12.390$  (9) Å. The crystal structure consists of two orthogonal and nonintersecting linear chains of  $\text{Hg}^{0.33+}$  cations passing through a lattice of octahedral  $\text{AsF}_6^-$  anions. The intrachain Hg–Hg distance of 2.64 (2) Å is derived from planes of diffuse scattering normal to  $a^*$  and  $b^*$ . Since the  $a$  and  $b$  axis lattice constants are not simple multiples of the Hg–Hg intrachain distance, the mercury chains are incommensurate with the tetragonal lattice; hence we have the apparent formula  $\text{Hg}_{2.86}\text{AsF}_6$ . These results are in essential agreement with a previously reported x-ray diffraction study. However, from the neutron diffraction data, we have established that the Hg chains are *not* strictly one-dimensional. The maximum room-temperature deviation from the chain axis is 0.07 (1) Å with neighboring chains distorted away from each other. The closest interchain Hg–Hg contact is 3.24 (2) Å. Furthermore, analytical data consistently indicate a stoichiometric empirical formula of  $\text{Hg}_3\text{AsF}_6$ . These results together with precise density measurements imply that the incommensurate structure is stabilized by anion vacancies, such that there are four formula weights of  $\text{Hg}_{2.86}(\text{AsF}_6)_{0.953}$  per unit cell.

### Introduction

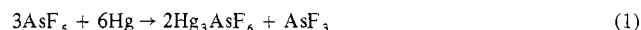
The properties of "low-dimensional" metals have been actively studied recently. Gillespie and co-workers<sup>2</sup> have reported the synthesis, structure, and properties of a novel  $\text{Hg}_{2.86}\text{AsF}_6$  compound, containing two orthogonal and nonintersecting linear chains of mercury atoms. From the x-ray study,<sup>2a</sup> diffuse planes of scattering intensity were observed normal to each chain direction, from which a Hg–Hg repeat distance of 2.64 (1) Å was obtained. The existence of the diffuse scattering indicated that the positions of the Hg atoms between neighboring chains are not correlated. Furthermore, the 2.64 Å repeat distance is incommensurate with the lattice dimensions ( $a = b = 7.54$  Å) such that the nonstoichiometric empirical formula  $\text{Hg}_{2.86}\text{AsF}_6$  was derived from the relationship  $7.54/2.64 = 2.86$ .

In order to investigate the physical properties of this material, we have developed procedures for the growth of large single crystals. The product analyzes as  $\text{Hg}_3\text{AsF}_6$ , as also reported by Brown et al.<sup>2a</sup> for what was reformulated as  $\text{Hg}_{2.86}\text{AsF}_6$  based on the x-ray study. To verify the unusual structural model and provide additional structural data we undertook a neutron diffraction study, for which the problem of the dominance of Hg scattering is greatly lessened, as are the effects of absorption. We include, in addition, a summary of analytical data and the results of precise density measurements which have led us to conclude that this mercury chain salt is a stoichiometric compound in an incommensurate

structure stabilized by anion vacancies.

### Experimental Section

**Synthesis.** The detailed procedures for the synthesis of large, silvery-golden crystals (up to  $35 \times 35 \times 2$  mm) of  $\text{Hg}_3\text{AsF}_6$  will be reported elsewhere.<sup>3</sup> They involve the reaction of a solution of  $\text{AsF}_5$  in liquid  $\text{SO}_2$  with a mercury surface confined in 2-mm i.d. capillary tubing. To summarize, crystals are prepared by reacting either  $\text{AsF}_5^{2a}$  or  $\text{Hg}_3(\text{AsF}_6)_2^{2c}$  with mercury in liquid  $\text{SO}_2$  according to eq 1 and



2, respectively. Elemental analyses of the compound (Table I) show that it has the stoichiometric composition  $\text{Hg}_3\text{AsF}_6$ .

In certain experiments large, silvery-golden crystals of apparent composition  $\text{Hg}_3\text{AsF}_6\text{AsF}_3$  (Table I) were formed instead of the usual  $\text{Hg}_3\text{AsF}_6$ . The exact conditions needed for the synthesis of  $\text{Hg}_3\text{AsF}_6\text{AsF}_3$  are not clear and are presently under investigation. It appears that the formation may be initially dependent on the concentration of  $\text{AsF}_3$  in the solution at the reaction site.

**Neutron Diffraction Data Collection.** A crystal of  $\text{Hg}_3\text{AsF}_6$  was mounted under argon in a sealed lead-glass capillary in a general orientation, and all data were collected using an Electronics-and-Alloys four-circle goniostat at the Argonne CP-5 reactor in a manner previously described.<sup>4</sup> The cell dimensions (see Table II) in the body-centered tetragonal space group  $I4_1/amd$  ( $D_{4h}^{19}$ , No. 141)<sup>5a</sup> were obtained from a least-squares fit of the angles  $2\theta$ ,  $\chi$ , and  $\phi$  of 18 strong reflections ranging in  $2\theta$  from 41 to 54° ( $\lambda$  1.142 (1) Å). Four forms of intensity data were measured for each crystal out to  $(\sin \theta)/\lambda =$

Table I. Analytical Data for Mercury Chain Compounds<sup>a</sup>

	% Hg	% As	% F	Total
Calcd for Hg <sub>3</sub> AsF <sub>6</sub>	76.11	9.47	14.42	100.00
Calcd for Hg <sub>2.86</sub> AsF <sub>6</sub>	75.23	9.82	14.95	100.00
Found <sup>b</sup>	76.00	9.62	14.54	100.16
	75.96	9.67	14.25	99.88
	76.31	9.31	14.13	99.75
	76.17	9.62	14.34	100.13
	75.95	9.59	14.57	100.11
Found <sup>c</sup>	75.83	9.52	14.61	99.96
Found (av of 6 analyses) <sup>e</sup>	76.04 (0.07)	9.55 (0.05)	14.41 (0.08)	100.00
Calcd for Hg <sub>3</sub> AsF <sub>6</sub> ·AsF <sub>3</sub>	65.23	16.24	18.53	100.00
Calcd for Hg <sub>2.86</sub> AsF <sub>6</sub> ·AsF <sub>3</sub>	64.13	16.75	19.12	100.00
Found <sup>b</sup>	65.95	15.69	18.24	99.88
	65.53	16.09	18.32	99.94
	64.99	16.15	18.31	99.45
	65.46	15.92	18.60	99.98
Found (av of 4 analyses) <sup>e</sup>	65.48 (0.20)	15.96 (0.10)	18.37 (0.08)	99.81
Found <sup>d</sup>	62.96	15.13	16.71	94.80

<sup>a</sup> All analyses were carried out by Galbraith Analytical Laboratories, Knoxville, Tenn. <sup>b</sup> This study. <sup>c</sup> Reference 2a. <sup>d</sup> Analysis of actual crystal after it had been used in the neutron diffraction studies. Ratio Hg:As:F = 3.1:2.0:8.7. The crystal had apparently undergone slight oxidation and/or hydrolysis during the structural studies as judged by the presence of some very small mercury droplets on and around the crystal. It is known that the compound reacts instantly with air. <sup>e</sup> Standard deviations are given in parentheses.

Table II. Crystal Data and Refinement Indices

	Hg <sub>3</sub> AsF <sub>6</sub>	Hg <sub>3</sub> AsF <sub>6</sub> ·AsF <sub>3</sub> <sup>a</sup>
Space group	<i>I</i> 4 <sub>1</sub> / <i>amd</i>	<i>I</i> 4 <sub>1</sub> / <i>amd</i>
<i>a</i> , Å	7.549 (5)	7.548 (7)
<i>c</i> , Å	12.390 (9)	12.355 (12)
<i>V</i> , Å <sup>3</sup>	706.1	703.9
<i>Z</i>	4	4
$\rho_{\text{exptl}}$ , g/cm <sup>3</sup>	7.06 (2)	
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup> <sup>b</sup>	7.04	
$\mu$ , cm <sup>-1</sup>	4.57	4.57
$g \times 10^{-4}$ <sup>c</sup>	0.70 (6)	0.31 (5)
No. of data measured	1138	924
No. of independent data	312	256
$R(F_o)$	0.078	0.094
$R(F_o^2)$	0.066	0.066
$R_w(F_o^2)$	0.089	0.094

<sup>a</sup> Formula obtained from elemental analyses (see Table I) although neutron diffraction results are identical with those for Hg<sub>3</sub>AsF<sub>6</sub>. <sup>b</sup> Based on four formula weights of Hg<sub>2.86</sub>(AsF<sub>6</sub>)<sub>0.94</sub> per unit cell. <sup>c</sup> Secondary extinction coefficient.<sup>2</sup>

0.72 using the  $\theta$ - $2\theta$  step-scan mode, with 0.1° step intervals and preset scan ranges of 50–62 steps. The data were corrected for absorption, equivalent reflections were averaged (see Table II), and a set of  $F_o^2$  values were obtained,<sup>6</sup> where  $F_o$  is the observed structure factor amplitude. The variances of  $F_o^2$  were calculated using the expression  $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.03F_o^2)^2$ , where  $\sigma_c^2(F_o^2)$  is determined from counting statistics and 0.03 is an added factor deduced from the 3% maximum variation of the two reference reflections which were measured periodically throughout the data collection.

**Solution and Refinement of the Structure.** The positions of the arsenic and fluorine atoms were obtained from Patterson synthesis maps. Refinement<sup>7</sup> of their positional and anisotropic thermal parameters led to discrepancy factors<sup>8</sup> of  $R(F_o) = 0.617$ ,  $R(F_o^2) = 0.854$ , and  $R_w(F_o^2) = 0.852$ . Fourier and difference-Fourier maps revealed cylinders of nuclear density with relatively little variation along the direction of the cylinder axis. Using the Brown et al. model<sup>2a</sup> of a one-dimensional Hg atom disorder, four Hg atoms with partial occupancy factors were placed at  $x \approx 0.03, 0.09, 0.16$ , and  $0.22$ . At a later stage in our refinement of the structure, it was found that a better fit to the observed Fourier maps was obtained with Hg atoms positioned at  $x = 0.0$  and  $0.5$  with three equally spaced atoms between. Furthermore, where crystallographically possible we have also allowed

Table III

Final Positional and Thermal Parameters for Hg <sub>3</sub> AsF <sub>6</sub>				
Atom	<i>x</i> <sup>a</sup>	<i>y</i>	<i>z</i>	<i>B</i> , <sup>b</sup> Å <sup>2</sup>
As	0.0	0.25	0.375	<i>c</i>
F(1)	0.0	0.25	0.2377 (2)	<i>c</i>
F(2)	0.6611 (3)	0.9111	0.875	<i>c</i>
Hg(1)	0.0	0.0	0.0	4.7 (2)
Hg(2)	0.0	0.062 (1)	0.0006 (7)	4.8 (1)
Hg(3)	0.0	0.121 (1)	0.0031 (7)	4.4 (1)
Hg(4)	0.0	0.1864 (9)	0.0046 (7)	3.9 (1)
Hg(5)	0.0	0.25	0.0059 (8)	4.0 (1)

Anisotropic Thermal Parameters ( $\times 10^4$ ) <sup>d</sup>						
Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
As	110 (5)	110	28 (1)	0	0	0
F(1)	248 (7)	418 (11)	31 (1)	0	0	0
F(2)	166 (4)	166	102 (2)	-44 (2)	-14 (3)	14

<sup>a</sup> *x*, *y* and *z* are fractional coordinates. <sup>b</sup> Isotropic temperature factors are of the form  $\exp(-B(\sin^2 \theta)/\lambda^2)$ . <sup>c</sup> Atoms refined anisotropically. <sup>d</sup> Anisotropic temperature factors are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

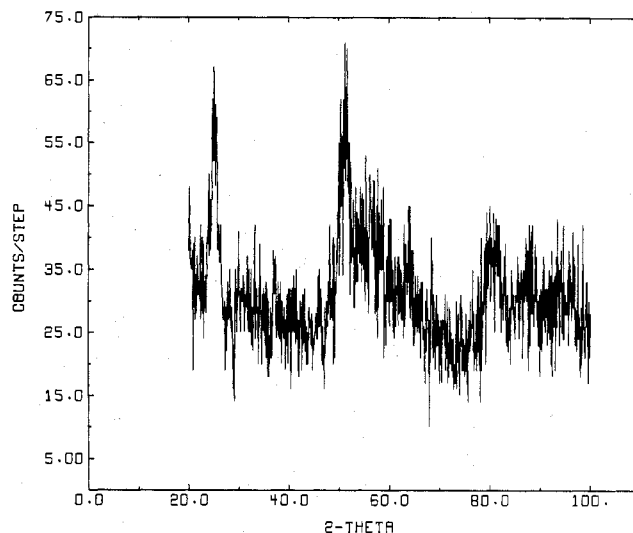
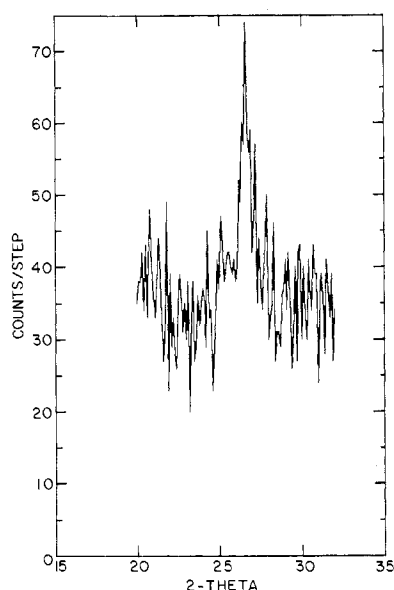


Figure 1. A  $\theta$ - $2\theta$  step scan showing peaks corresponding to the first-, second-, and third-order diffuse planes of scattering normal to the  $a^*$  axis. The  $a^*$  axis is slightly offset from reflecting position in order to avoid the  $h00$  Bragg reflections.

the *z* coordinates for the mercury atoms to vary, whereas they were fixed equal to zero in the x-ray structural solution.<sup>2a</sup> Due to the large correlations among the Hg atomic positions and their  $\beta_{11}$ 's, it was not possible to refine their thermal parameters anisotropically. The As and F multipliers were adjusted to obtain four formula weights of Hg<sub>2.86</sub>(AsF<sub>6</sub>)<sub>0.95</sub> per unit cell. The data were also corrected for secondary extinction<sup>9,10</sup> with correction factors ranging from 1.00 to 2.20 although only 11 reflections had factors greater than 1.25. The final discrepancy indices based on the last least-squares refinement are given in Table II. Table III lists the positional and thermal parameters of the atoms. The final difference-Fourier maps were featureless with the highest residual peaks 2.1% or less than that of the As atom.

A neutron diffraction study of a crystal of the apparent AsF<sub>3</sub> adduct gave results (see Table II) identical with those for Hg<sub>3</sub>AsF<sub>6</sub> even though the elemental analysis of the crystal after it had been used in the neutron diffraction study indicates the formula Hg<sub>3</sub>AsF<sub>6</sub> (see Table I). It seems possible that the compound consists of small crystallites of Hg<sub>3</sub>AsF<sub>6</sub> which are surrounded by AsF<sub>3</sub> in microscopic cracks and voids. Experimental studies have shown no observable differences in electrical or optical properties of crystals of the two different compositions.

**Diffuse Scattering.** The planes of scattering intensity were easily observed by  $\theta$ - $2\theta$  step-scans in numerous directions. This confirmed that indeed there were planes (rather than streaks) oriented per-



**Figure 2.** A  $\theta$ - $2\theta$  step scan along the (110) vector with lattice parameters  $a' = a$  and  $b' = 2.64$  Å. The peak corresponds to the first-order diffuse plane normal to the  $a^*$  axis.

pendicular to the  $a^*$  and  $b^*$  reciprocal axes. A scan, slightly offset from the  $a^*$  axis to avoid Bragg reflections, is shown in Figure 1, with peaks corresponding to the first-, second-, and third-order planes. Figure 2 is a (110) scan using the lattice parameters  $a' = a$  and  $b' = 2.64$  Å. The value of  $b'$  calculated from the peak at  $2\theta = 26.6^\circ$  is 2.63 Å, which is in good agreement with 2.64 (1) Å reported by Brown et al.<sup>2a</sup> and 2.665 (5) Å obtained by Hastings et al.<sup>11</sup>

### Discussion

As shown in Figure 3, the crystal structure consists of octahedral  $\text{AsF}_6^-$  anions with linear chains of Hg atoms parallel to the  $a$  and  $b$  directions. Up to this point the structural solution is in essential agreement with that obtained from the previous x-ray analysis.<sup>2a</sup> The two independent As-F distances are (see Table IV) As-F(1) = 1.702 (2) Å and As-F(2) = 1.720 (2) Å, and the shortest F...Hg contact is 2.87 (1) Å.

The evidence for the existence of Hg chains with Hg-Hg = 2.64 Å,<sup>11</sup> and no correlation of Hg positions between chains,

**Table IV.** Selected Interatomic Distances (Å) for  $\text{Hg}_3\text{AsF}_6$

As-F(1)	1.702 (2)	Hg(5)-Hg(5) <sup>b</sup>	3.24 (2)
As-F(2)	1.720 (2)	F(1)-Hg(5)	2.87 (1)
Hg-Hg <sup>a</sup>	2.64 (2)	F(2)-Hg(3)	2.981 (5)

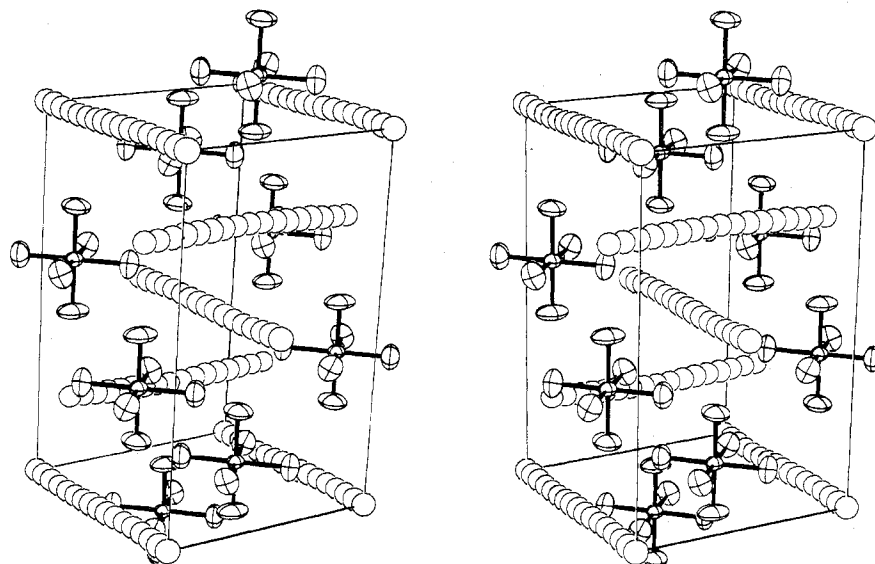
<sup>a</sup> Intrachain Hg-Hg separation derived from the diffuse-scattering planes. The esd is not experimentally determined.

<sup>b</sup> Closest interchain Hg-Hg separation. If the chains are assumed to be strictly one-dimensional, then interchain Hg-Hg =  $c/4 = 3.098$  (9) Å.

is obtained from the one-dimensional disorder observed in Fourier maps based on the Bragg data and the planes of diffuse-scattering intensity. We have integrated the peaks obtained from scans through the planes and find decreasing intensities at higher scattering angle (see Figure 1), rather than increasing intensities found in the Peierls distorted one-dimensional metals.<sup>12</sup> This is further evidence that the scattering is due to one-dimensional chains with equivalent repeat distances and is not due to satellite reflections resulting from a one-dimensional distortion of a three-dimensional lattice.

The correlation length within each chain can be determined from the reciprocal space width of the diffuse scattering normal to the planes. From the scan in Figure 2, we estimate a half-height peak width of  $\sim 1.6^\circ$  in  $2\theta$ , which leads to  $\Delta^* = 0.0239$  Å<sup>-1</sup>. This gives a correlation length of  $\Delta = 1/\Delta^* = 41.8$  Å, or about 16 Hg-Hg separations. However, the average Bragg reflections in this region have widths of 1.6–2.0°, and since in general  $(\Delta^*_{\text{obsd}})^2 = (\Delta^*_{\text{Bragg}})^2 + (\Delta^*_i)^2$ ,<sup>13</sup> there is essentially no contribution due to a short correlation length. Therefore, the true correlation length is probably many times longer than 41.8 Å.

It should be noted that the mercury chains are *not* crystallographically required to be exactly linear; i.e., they are not required to be strictly one-dimensional. Except for the mercury atoms situated at the origin (and symmetry-related positions) of the unit cell, it is possible to vary two coordinates for each mercury atom. As seen in Figure 3, refinement of these coordinates results in a slight buckling of the mercury chains. The maximum room-temperature deviation from the chain axis in the  $c$  direction is 0.07 (1) Å and occurs at the point of nearest contact with a second chain such that the two chains are distorted *away* from each other. Consequently, the closest interchain Hg-Hg contact is 3.24 (2) Å, whereas if the chains were strictly linear it would be  $c/4 = 3.098$  (9) Å.



**Figure 3.** A stereoscopic view of the unit cell of  $\text{Hg}_3\text{AsF}_6$  showing the disordered model for the Hg chains. Each Hg position is only partially occupied. The thermal ellipsoids are scaled to 50% probability. It should be noted that the mercury chains are not required crystallographically to be linear, such that a slight buckling of the chains is observed, with a maximum deviation from the chain axis of 0.07 (1) Å.

The buckling of the Hg chains also implies that the number of Hg atoms per *a* and *b* unit-cell edge is not exactly the ratio of the *a*-axis length to the Hg–Hg intrachain distance obtained from the diffuse planes but is actually very slightly greater. Hastings et al.<sup>11</sup> have observed that the repeat distance of the diffuse planes (and, therefore, the Hg–Hg distance) remains constant although the tetragonal lattice parameters contract as the temperature is lowered. Assuming that the stoichiometry within an isolated single crystal is not temperature dependent (i.e., the crystal does not reversibly lose Hg upon cooling and gain Hg upon heating), this indicates that the magnitude of the buckling must increase at low temperature in order to accommodate the same number of Hg atoms per unit cell.

From a study of the electrical transport properties it has been observed that at room temperature the conductivity is 10<sup>2</sup> times greater in the chain directions than along *c*.<sup>2b,14</sup> but near 4 K only the *c*-axis resistivity drops abruptly at the onset of superconductivity.<sup>14</sup> From the structural point of view we note that the 3.24 (2) Å distance between Hg chains in the *c* direction indicates a significant degree of partial metal–metal bonding. For comparison, the internuclear distance in metallic mercury is 3.00 Å.

The conflict between the elemental analyses data, which indicate an empirical formula of Hg<sub>3</sub>AsF<sub>6</sub>, and the structural results, which indicate only 2.86 mercury atoms per chain in a unit cell, appears to be resolved by the existence of a defect structure with approximately one AsF<sub>6</sub><sup>-</sup> in twenty missing from the structure. The resulting chemical formula expressed per average unit cell would be (using the highest precision Hg–Hg distance of 2.66 Å<sup>11</sup>) Hg<sub>2.82</sub>(AsF<sub>6</sub>)<sub>0.94</sub>, i.e., 0.94 (Hg<sub>3</sub>AsF<sub>6</sub>). Since the anion vacancies are presumably random, this model is consistent with both the neutron diffraction and analytical data.

High-precision density measurements have confirmed this picture. The measured density was found to be  $\rho = 7.06 \pm 0.02$  g/cm<sup>3</sup> in close agreement with the calculated value  $\rho_{\text{calcd}} = 7.04$  g/cm<sup>3</sup> based on the structure and the formula Hg<sub>2.82</sub>(AsF<sub>6</sub>)<sub>0.94</sub>.<sup>3</sup> An alternative suggestion of 6% excess mercury disordered in the lattice (Hg<sub>2.82</sub>AsF<sub>6</sub> + 0.18Hg) with no anion defects would lead to a density of 7.49 g/cm<sup>3</sup>, far outside the limits of error.<sup>3</sup> Thus, this mercury-chain metal is a stoichiometric compound in an incommensurate structure stabilized by anion vacancies.

**Acknowledgment.** Research at ANL was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. Partial support of A.J.S. by the National Science Foundation (Grant No. CHE 76-07409 to

Argonne National Laboratory) is gratefully acknowledged. Work at the University of Pennsylvania was supported by NSF Grants CHE-73-04771-A03 and CHE-77-02207-A01 and by the NSF Materials Research Laboratory (Grant No. DMR 76-00678).

**Registry No.** Hg<sub>3</sub>AsF<sub>6</sub>, 59539-90-1.

**Supplementary Material Available:** A listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) (a) Argonne National Laboratory. (b) Department of Chemistry, University of Pennsylvania. (c) Department of Physics, University of Pennsylvania.
- (2) (a) I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, **52**, 791 (1974); (b) B. D. Cutforth, W. R. Datars, A. Van Schyndel, and R. J. Gillespie, *Solid State Commun.*, **21**, 377 (1977); (c) B. D. Cutforth and R. J. Gillespie, private communication, 1976.
- (3) N. D. Miro, A. G. MacDiarmid, A. J. Heeger, A. F. Garito, C. K. Chiang, A. J. Schultz, and J. M. Williams, submitted for publication in *J. Inorg. Nucl. Chem.*
- (4) J. M. Williams, K. D. Keefer, D. M. Washecheck, and N. P. Enright, *Inorg. Chem.*, **15**, 2446 (1976).
- (5) (a) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969; (b) *ibid.*, Vol. IV, 1974, p 270.
- (6) Computer programs used in this study: automatic indexing and Bravais lattice determination, BLIND (R. A. Jacobson, *J. Appl. Crystallogr.*, **9**, 115 (1976)); data reduction and absorption corrections, DATALIB; data averaging and sort, DATASORT; least-squares refinement, ORXFLS; Fourier summation, FORDAP; error analysis of distances and angles, ORPFE3; structure plotting, ORTEPII.
- (7) All least-squares refinements were based on the minimization of  $\sum w_i |F_o^2 - S^2 F_c^2|$ , where *S* is the scale factor and the individual weights  $w_i = 1/\sigma^2(F_c^2)$ . The neutron scattering amplitudes<sup>2b</sup> used in this study were  $b_{\text{Hg}} = 1.27$ ,  $b_{\text{As}} = 0.64$ , and  $b_{\text{F}} = 0.57$  (all in units of 10<sup>-12</sup> cm).
- (8)  $R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $R(F_c^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2$ , and  $R_w(F_o^2) = [\sum w_i |F_o^2 - F_c^2|^2 / \sum w_i F_o^4]^{1/2}$ .
- (9) The Zachariasen approximation<sup>10a</sup> was used for the overall isotropic *g* parameter as defined and scaled by Coppens and Hamilton.<sup>10b</sup> The  $|F_o|$  values were corrected for extinction from the expression  $|F_{\text{obs}}| = |F_o| \{1 + T(2g)\lambda^3 |F_o|^2 V^2 \sin^2 \theta\}^{-1/4}$ , where  $|F_o|$  is on an absolute scale, and  $\lambda$  is the wavelength (Å), *g*, the refined extinction parameter, *T*, the mean absorption-weighted path length in the crystal in centimeters (calculated simultaneously during the computation of absorption corrections), and *V*, the unit cell volume (Å<sup>3</sup>).
- (10) (a) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); (b) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).
- (11) High-precision elastic neutron scattering measurements at Brookhaven National Laboratory gave a Hg–Hg repeat distance of 2.665 (5) Å at room temperature: J. M. Hastings, J. P. Pouget, G. Shirane, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1484 (1977).
- (12) A. J. Schultz, G. D. Stucky, J. M. Williams, T. R. Koch, and R. L. Maffly, *Solid State Commun.*, **21**, 197 (1977).
- (13) A. Guinier, "X-Ray Diffraction", W. H. Freeman, San Francisco, Calif., 1963, p 143.
- (14) C. K. Chiang, R. Spal, A. Denenstein, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, *Solid State Commun.*, **22**, 293 (1977); R. Spal, C. K. Chiang, A. Denenstein, A. J. Heeger, N. D. Miro, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 650 (1977).