Supporting Information

$(C_8H_{22}N_4Zn)_2Ge_7O_{14}(OH)F_3$: A One-Dimensional Zinc Germanate Containing Hollow Columns with an 18-Membered Window

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Figures

Figure S1. The observed powder X-ray diffraction pattern (**a**), and a simulated one based on the results from single-crystal X-ray diffraction (**b**) of $(C_8H_{22}N_4Zn)_2Ge_7O_{14}(OH)F_3$ (denoted as **1**).

Figure S2. A photo of crystals of **1**.

Figure S3. The total reflection X-ray fluorescence spectrum of **1**.

Figure S4. The infrared spectrum of **1** (KBr pellet method).

Figure S5. The thermogravimetric analysis curve of **1** measured under flowing nitrogen gas at a heating rate of 10 $^{o}C \cdot min^{-1}$.

Tables

Table S1. The Crystallographic data for **1**.

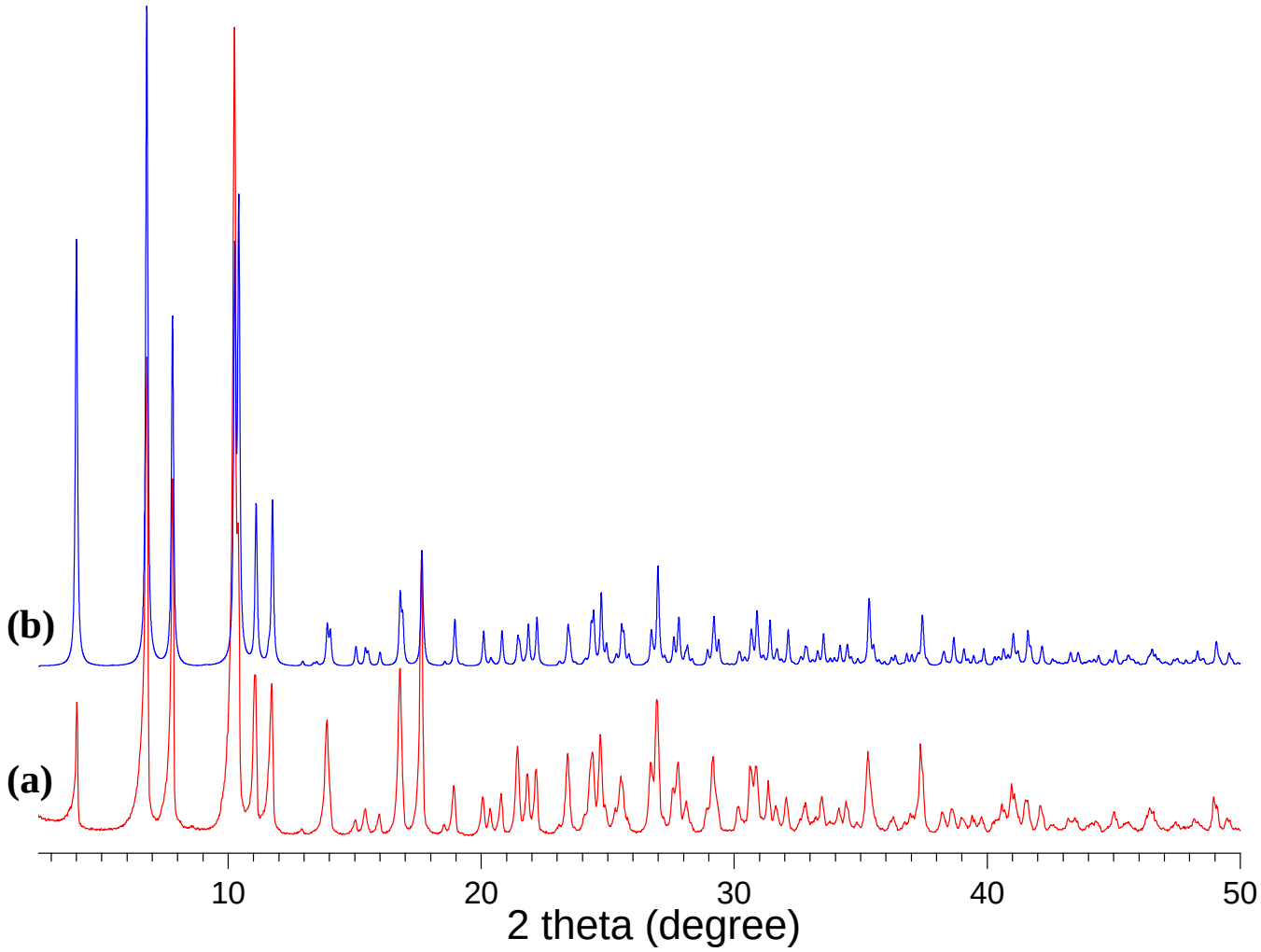

Figure S1

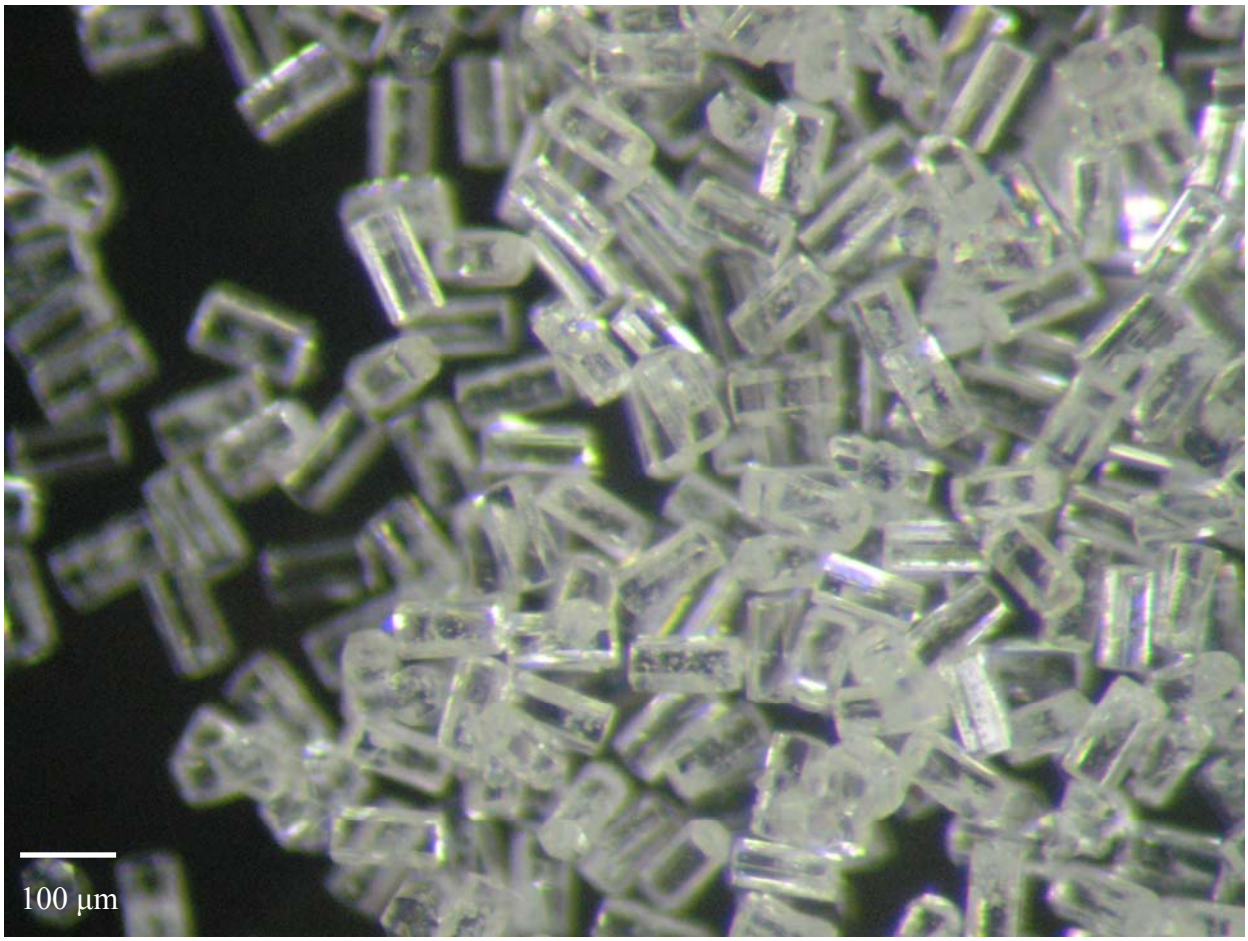

Figure S2

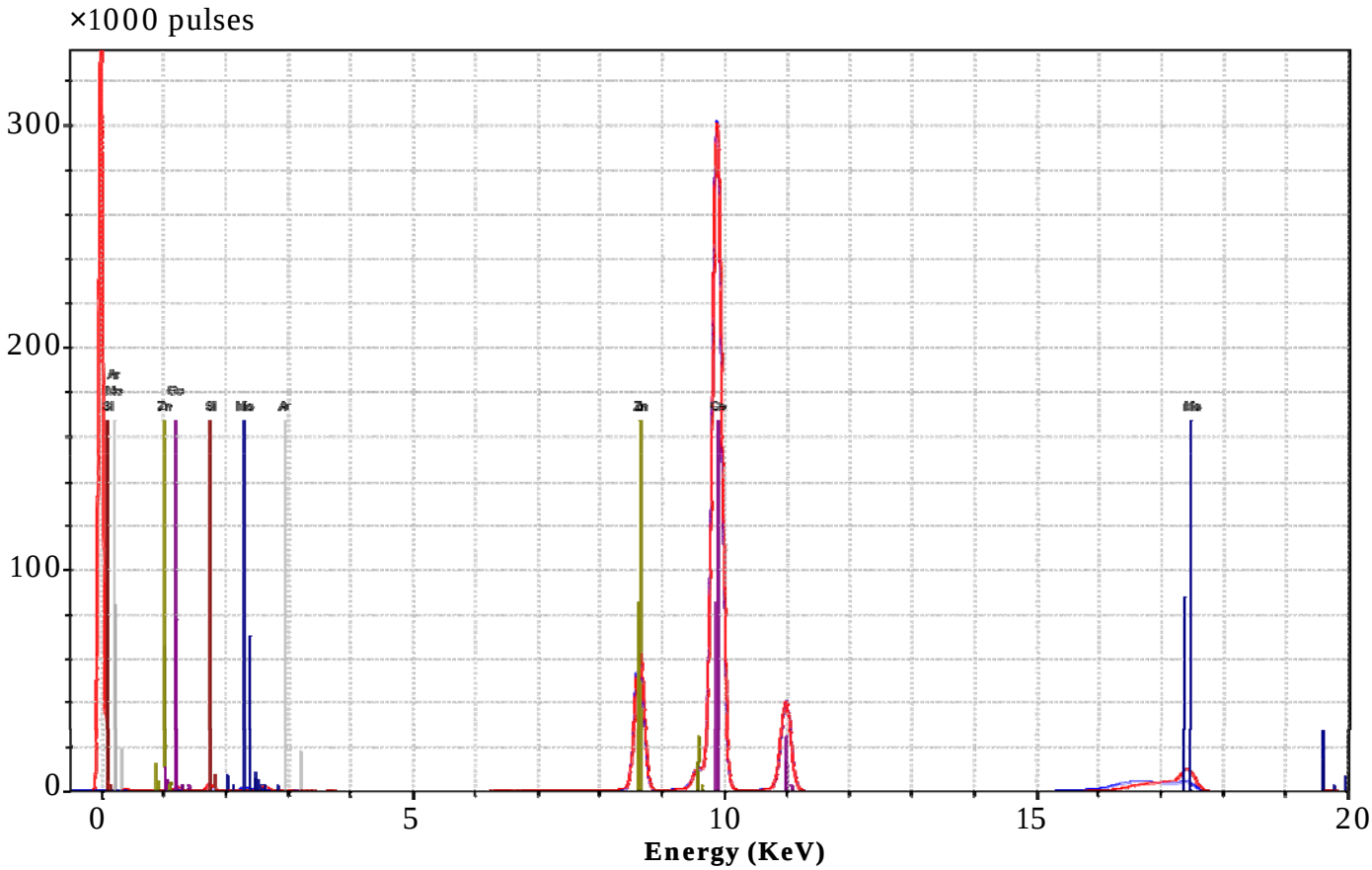

Figure S3

A powder sample of **1** was dissolved by heating it in a mixture of ethylenediamine and ethylene glycol (volume ratio of 1 : 1) at 160 ^{o}C for 10 hours. The total reflection X-ray fluorescence analysis was performed in a total reflection X-ray fluorescence spectrometer equipped with Mo anode running at voltage of 50 kV, current of 0.602 mA, and exposure time of 600 sec. $K_{\alpha 1,\alpha 2}$ lines of Ge and Zn elements were used for analysis.

Elements	Relative Concentration (ppm)	Molar Ratio of Ge/Zn
Ge	794270	**3.48**
Zn	205730	

In addition to the signals of Ge and Zn elements, some weak signals of Mo from the X-ray source, Si from the sample holder, and Ar from air also appeared in the spectrum.

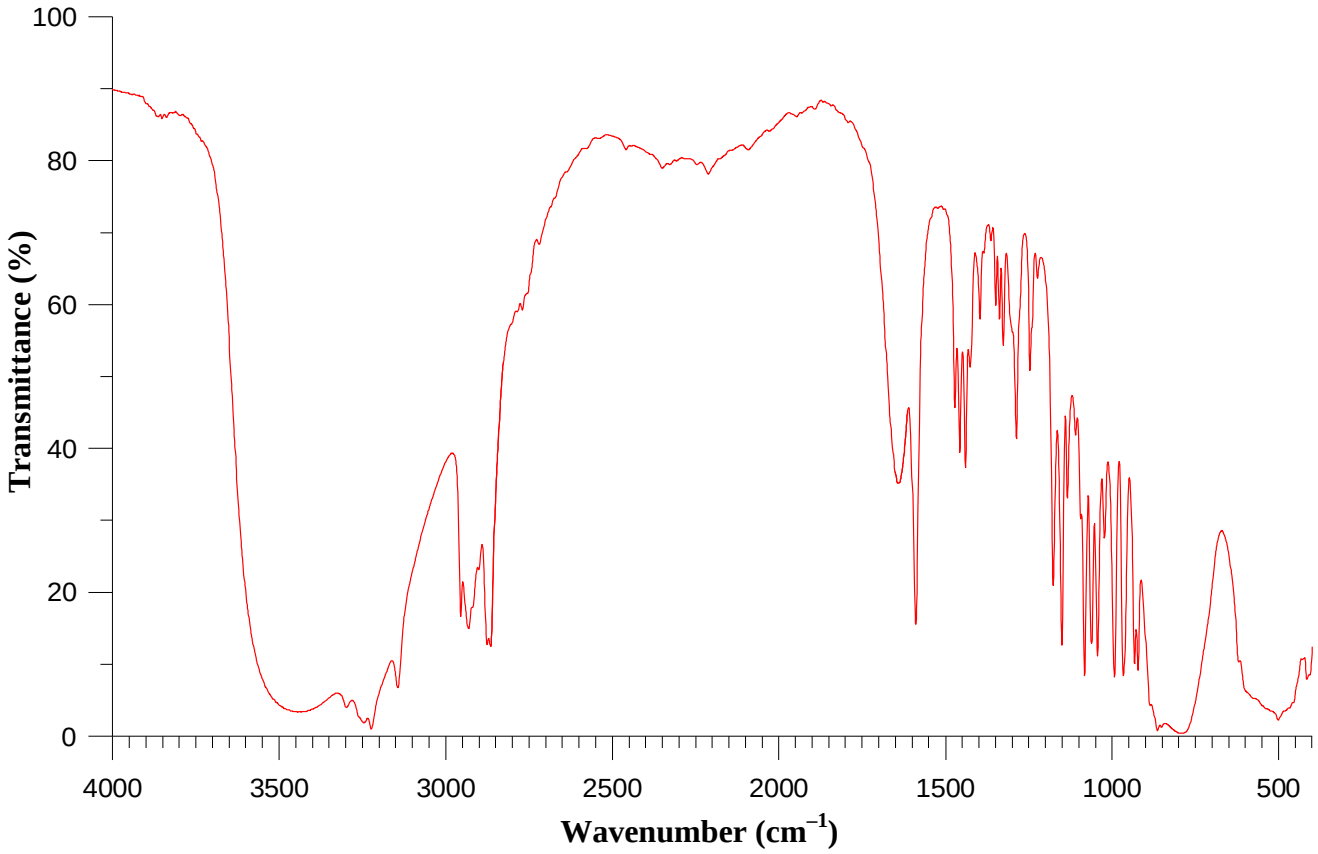

Figure S4

The FTIR spectrum of **1** was measured on a Jasco FTIR-4200 series spectrophotometer over the range 4000–400 cm^{-1} at the resolution of 4 cm^{-1} using the KBr pellet method.

The strong band from 3600 to 3143 cm^{-1} is the stretching vibrations of OH and N–H groups in **1**. The sharp bands centered at 2954, 2930, 2876 and 2861 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of CH_2 groups.[1-4] The bands at 1640 and 1598 cm^{-1} are the asymmetric and symmetric bending of H–N–H groups. The sharp bands from 1472 to 1223 cm^{-1} are the bending, twisting and wagging of CH_2 group and those from 1177 to 922 cm^{-1} are the stretching vibrations of C–N groups in the coordinated amine.[2] The broad, strong bands centered at 864 to 787 cm^{-1} can be assigned to the vibrations of Ge–O and Ge–F bonds.[5] The bands at 500 and 406 cm^{-1} are attributed to the symmetrical stretching and bending vibrations of the Ge–O bonds.[6]

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(1) Nguyen, Q. B.; Lii, K.-H. *Dalton Trans.* **2011**, *40*, 10830–10832.

(2) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*. Academic Press: New York, 1963, pp 245–281.

(3) Zhang, H.-X.; Zhang, J.; Zheng, S.-T.; Yang, G.-Y. *Inorg. Chem.* **2003**, *42*, 6595–6597.

(4) Conradsson, T.; Zou, X.; Dadachov, M. S. *Inorg. Chem.* **2000**, *39*, 1716–1720.

(5) Beitone, L.; Loiseau, T.; Férey, G. *Inorg. Chem.* **2002**, *41*, 3962–3966.

(6) Davidson, G. In *Spectroscopic Properties of Inorganic and Organometallic Compounds*; Davidson, G., Dillon, K. B., Rankin, D. W. H., Robertson, H. E., Reporters; RSC: England, 2005; Vol. 37, pp. 17–69.

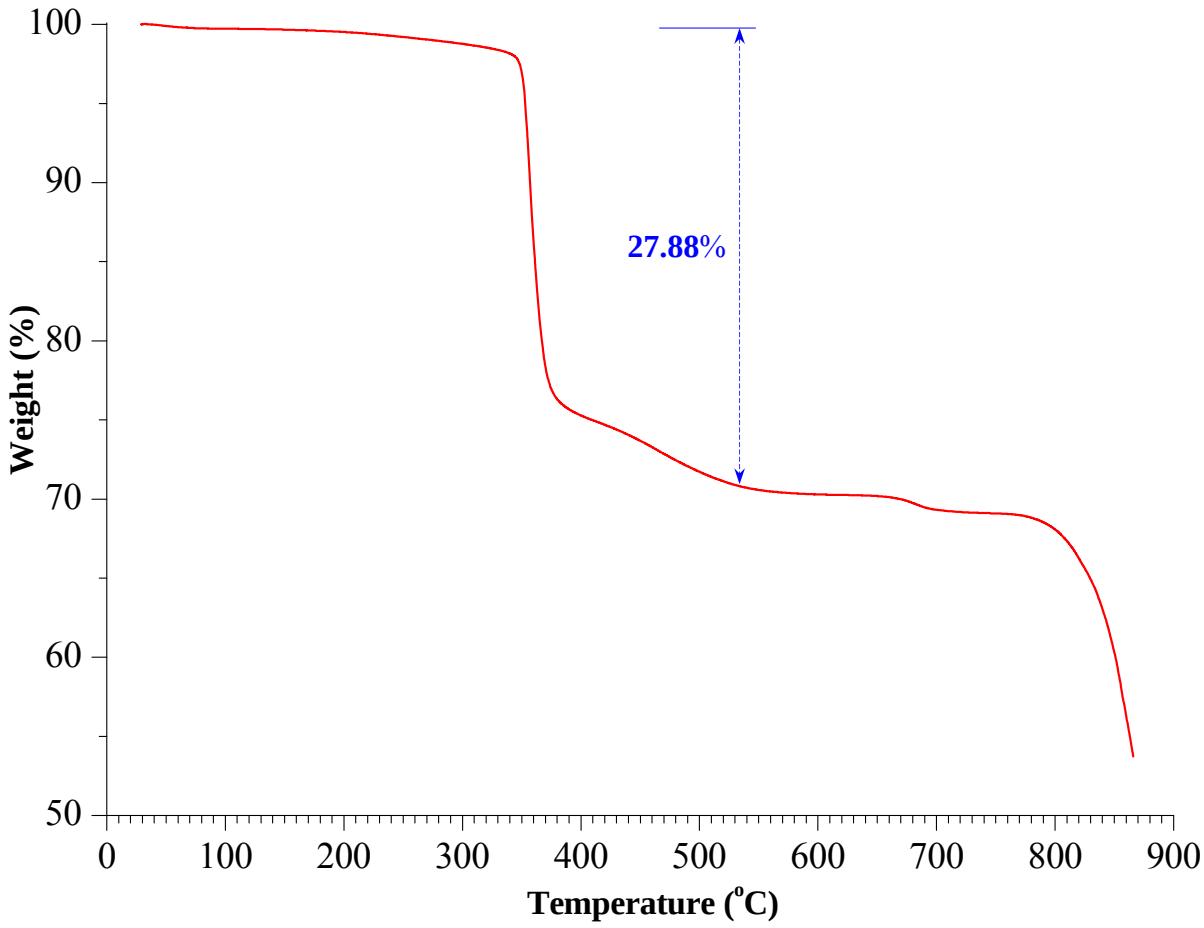
100
90
80
70
60
50
Weight (%)
27.88%
0
100
200
300
400
500
600
700
800
900
Temperature (°C)

Figure S5

Table S1. The Crystallographic data for **1**

Empirical formula	$C_{16}H_{45}N_8F_3Ge_7O_{15}Zn_2$
Formula weight	1285.47
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$R\bar{3}$ (No. 148)
Unit cell dimensions	a = 46.5858(13) Å; $\alpha = 90^o$
	b = 46.5858(13) Å; $\beta = 90^o$
	c = 8.8708(3) Å; $\gamma = 120°$
Volume	16672.5(9) $Å^3$
Z	18
Density (calculated)	2.305 g/cm^3
Absorption coefficient	6.952 mm^{-1}
F(000)	11304
Crystal size	0.1 × 0.04 × 0.04 mm^3
Theta range for data collection	2.31 to 28.36°
Index ranges	$-62 \le h \le 62$, $-56 \le k \le 58$, $-11 \le l \le 9$
Reflections collected	29584
Independent reflections	9234 [R(int) = 0.0625]
Completeness to theta = 28.36°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9234 / 0 / 461
Goodness-of-fit on F^2	1.016
Final R indices[(1)] [$I > 2\sigma(I)$]	R_1 = 0.0396, wR_2 = 0.0923
R indices (all data)	R_1 = 0.0762, wR_2 = 0.1047
Extinction coefficient	0.000018(5)
Largest diff. peak and hole	1.565 and – 0.753 e.$Å^{-3}$

[(1)] $R_1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$.

$wR_2 = [\Sigma\, w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [Max(F_o^2,0) + 2(F_c)^2]/3$, where a = 0.0420 and b = 61.06.