

atom forms a decahedron with two O(1), four O(2) and one Cl atoms. The Cl atoms is linearly bonded with two Ca atoms. The structure type of wadalite is completely different from that of grossular; wadalite is classified as a framework aluminosilicate, whereas grossular garnet is classified as a monosilicate (or nesosilicate). However, the atomic positions of grossular and wadalite are closely related to each other (Table 1). Thus, wadalite and grossular have similar cell dimensions and diffraction intensities. Since the powder diffraction pattern of wadalite cannot be distinguished from that of grossular, some

wadalites may have been wrongly identified as grossular.

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## A New Layered $\text{ZnIn}_2\text{S}_4$ -(IIIa) Polytype: Structure of $\text{FeCr}_{0.8}\text{Ga}_{1.2}\text{Se}_4$

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**Abstract.** Chromium gallium iron selenide,  $\text{FeCr}_{0.8}\text{Ga}_{1.2}\text{Se}_4$ ,  $M_r = 496.95$ , rhombohedral,  $R\bar{3}m$ ,  $a = 3.8284$  (6),  $c = 37.914$  (5) Å,  $V = 481.2$  Å<sup>3</sup>,  $Z = 3$ ,  $D_x = 5.14$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7093$  Å,  $\mu = 308.70$  cm<sup>-1</sup>,  $F(000) = 655$ ,  $T = 293$  K,  $R = 0.049$  for 265 reflections. The structure is a novel centrosymmetric  $\text{ZnIn}_2\text{S}_4$ -(IIIa) polytype with an unusual  $(cM'hM^o hM'c)_3$  stacking, which results from the random distribution of the tetrahedrally coordinated metal atoms.

**Introduction.** X-ray powder diffraction analyses of the system  $\text{FeCr}_{2x}\text{Ga}_{2-2x}\text{Se}_4$  (Siwert & Lutz, 1987) have revealed a large range of solid solutions ( $0.65 < x < 0.8$ ). Because of the composition of the solid solutions and the site preference of the metals involved, the structure of these novel compounds was suggested to be that of  $\text{ZnIn}_2\text{S}_4$ -(IIIa) type. The end-member phase  $\text{FeCr}_2\text{Se}_4$  possesses a defect NiAs structure with all metal ions in an octahedral environment contrary to  $\text{FeGa}_2\text{Se}_4$ , the other end-member phase, where all metal ions are tetrahedrally coordinated (defect zinc-blende type). Therefore, samples of composition  $\text{FeCrGaSe}_4$  should exhibit a tetrahedral coordination of Fe and Ga and an octahedral coordination of Cr. This cation distribution should be proved by an X-ray single-crystal measurement.

**Experimental.** Single crystals of  $\text{FeCr}_{0.8}\text{Ga}_{1.2}\text{Se}_4$  were grown by recrystallization of powdery material at

1073 K for two weeks using  $\text{AlCl}_3$  as mineralization agent (Stingl, 1991). The composition of the crystal obtained differs from that of the starting material. A plate-like crystal  $0.2 \times 0.2 \times 0.02$  mm was transferred to an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo  $K\alpha$  radiation was used. Unit-cell parameters were obtained from least-squares treatment of 25 reflections ( $16.9 \leq 2\theta \leq 34.9^\circ$ ). The intensity data of 1433 reflections ( $2\theta \leq 70^\circ$ ;  $\omega$ - $2\theta$  scan;  $0 \leq h \leq 6$ ,  $0 \leq k \leq 6$ ,  $0 \leq l \leq 60$ ) were corrected for Lorentz and polarization effects with the Enraf–Nonius SDP (B. A. Frenz & Associates, Inc., 1982). Of the 330 unique reflections ( $R_{\text{int}} = 0.036$ ), 65 with  $I \leq 3\sigma_I$  ( $\sigma_I$  from counting statistics) were considered unobserved. Empirical absorption corrections were applied using nine reflections in the  $2\theta$  range  $24.8 \leq 2\theta \leq 58.8^\circ$ . The minimum and maximum transmission values were 20.0 and 99.5%. 030, 220,  $\bar{3}00$  were chosen as standard reflections in order to control intensity variations. The variations in intensity throughout the data collection were less than 1%. The structure was refined by full-matrix least-squares techniques including the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ( $N_p = 13$ ), using scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1974, Vol. IV) including the terms for anomalous dispersion. Initial parameters for the atomic positions were taken from a Patterson map based on a  $\text{ZnIn}_2\text{S}_4$ -(IIIa) structure type (Razzetti, Lottici & Zanotti, 1984). The final

refinements based on the  $F$  magnitudes of 265 observations with  $I \geq 3\sigma_I$  resulted in  $R = 0.049$ ,  $wR = 0.039$  ( $w = 1/\sigma_F^2$ ),  $S = 3.900$ . The secondary-extinction parameter of FeCr<sub>0.8</sub>Ga<sub>1.2</sub>Se<sub>4</sub> converged to  $4.3(2) \times 10^{-6}$ . The ratios of the maximum least-squares shifts to the e.s.d.'s in the final cycle were  $< 0.001$ ; the maximum and minimum heights in the final difference Fourier syntheses were  $-1.59$  and  $1.76 \text{ e } \text{\AA}^{-3}$ . The final atomic coordinates and thermal parameters are given in Table 1, selected bond lengths and angles in Table 2.\*

**Discussion.** The crystal structure of FeCr<sub>0.8</sub>Ga<sub>1.2</sub>Se<sub>4</sub> is a hitherto unknown centrosymmetric polytype of the layered non-centrosymmetric ZnIn<sub>2</sub>S<sub>4</sub>-(IIIa) structure type (Fig. 1). This new structure type is obviously a result of the equal occupation of the two

tetrahedral voids in the close-packed framework of Se atoms. Therefore, contrary to the ZnIn<sub>2</sub>S<sub>4</sub>-(IIIa) structure, a centrosymmetric structure is observed. The Cr atoms with the highest octahedral site preference share the octahedral site [3(b)] together with part of the Fe atoms; the Ga atoms and the second part of the Fe atoms occupy the tetrahedral site

\* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55531 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1004]

Table 1. Fractional coordinates (0,0,z) and anisotropic displacement parameters ( $\text{\AA}^2 \times 10^{-2}$ ) with e.s.d.'s in parentheses for  $M^o M_2^i \text{Se}_4$

$$M^o = 0.8\text{Cr} + 0.2\text{Fe}, \quad M^i = 0.6\text{Ga} + 0.4\text{Fe}. \quad U_{22} = U_{11}, \quad U_{12} = \frac{1}{2}U_{11}, \\ U_{13} = U_{23} = 0.$$

Site (symmetry)	z	$U_{11}$	$U_{33}$
$M^o$ 3(b) (3m)	0.5	0.131 (6)	0.094 (8)
$M^i$ 6(c) (3m)	0.06894 (3)	0.110 (3)	0.164 (5)
Se(1) 6(c) (3m)	0.13166 (3)	0.120 (3)	0.138 (4)
Se(2) 6(c) (3m)	0.29136 (3)	0.107 (3)	0.193 (5)

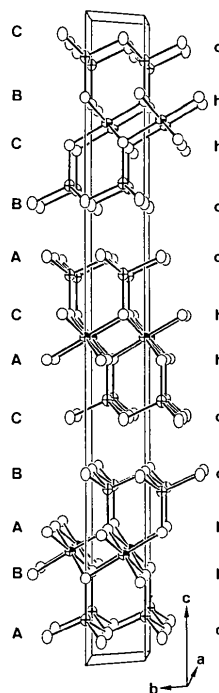


Fig. 1. Structure of  $M^o M_2^i \text{Se}_4$ , viewed along [100] and drawn at the 95% level (Johnson, 1976).

Table 2. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $M^o M_2^i \text{Se}_4$

			Symmetry
$M^o$ —Se(1)	6 ×	2.578 (1)	(i)–(xiv), (i)–(xv), (i)–(xvi), (i)–(xvii), (i)–(xviii), (i)–(xix)
$M^i$ —Se(1)	1 ×	2.379 (2)	(i)–(i)
$M^i$ —Se(2)	3 ×	2.436 (1)	(i)–(viii), (i)–(ix), (i)–(x)
Se(1)—Se(1)	6 ×	3.828 (1)	e.g. (i)–(ii), (i)–(iii)
Se(1)—Se(1)	3 ×	3.453 (1)	(i)–(vii), (i)–(ix), (i)–(x)
Se(1)—Se(2)	3 ×	4.056 (1)	(i)–(viii), (i)–(ix), (i)–(x)
Se(2)—Se(2)	6 ×	3.828 (1)	e.g. (i)–(ii), (i)–(iii)
Se(2)—Se(2)	3 ×	3.874 (1)	(i)–(xiv), (i)–(xv), (i)–(xvi)
$M^o$ — $M^o$	6 ×	3.828 (1)	(i)–(ii), (i)–(iii), (i)–(iv), (i)–(v), (i)–(vi), (i)–(vii)
$M^i$ — $M^i$	6 ×	3.828 (1)	(i)–(ii), (i)–(iii), (i)–(iv), (i)–(v), (i)–(vi), (i)–(vii)
Se(1)— $M^o$ —Se(1)	6 ×	95.89 (2)	(xiv)–(i)–(xv), (xiv)–(i)–(xvi), (xv)–(i)–(xvi)
Se(1)— $M^o$ —Se(1)	6 ×	84.11 (2)	(xvii)–(i)–(xviii), (xvii)–(i)–(xix), (xviii)–(i)–(xix)
Se(1)— $M^o$ —Se(1)	6 ×	84.11 (2)	(xiv)–(i)–(xvii), (xiv)–(i)–(xviii), (xv)–(i)–(xvii)
Se(1)— $M^i$ —Se(2)	3 ×	114.83 (4)	(xv)–(i)–(xix), (xvi)–(i)–(xviii), (xvi)–(i)–(xix)
Se(2)— $M^i$ —Se(2)	3 ×	103.62 (4)	(i)–(i)–(viii), (i)–(i)–(ix), (i)–(i)–(x)
$M^o$ —Se(1)— $M^o$	3 ×	95.89 (3)	(viii)–(i)–(ix), (viii)–(i)–(x), (ix)–(i)–(x)
$M^i$ —Se(2)— $M^i$	3 ×	103.62 (4)	(xi)–(i)–(xii), (xi)–(i)–(xiii), (xii)–(i)–(xiii)
			(viii)–(i)–(ix), (viii)–(i)–(x), (ix)–(i)–(x)

Symmetry code: (i)  $x, y, z$ ; (ii)  $1 + x, 1 + y, z$ ; (iii)  $1 + x, y, z$ ; (iv)  $x, 1 + y, z$ ; (v)  $x, -1 + y, z$ ; (vi)  $-1 + x, -1 + y, z$ ; (vii)  $-1 + x, -1 + y, z$ ; (viii)  $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$ ; (ix)  $-\frac{1}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$ ; (x)  $-\frac{1}{3} - x, -\frac{2}{3} - y, \frac{1}{3} - z$ ; (xi)  $\frac{1}{3} + x, \frac{2}{3} + y, -\frac{1}{3} + z$ ; (xii)  $\frac{1}{3} + x, -\frac{1}{3} + y, -\frac{1}{3} + z$ ; (xiii)  $-\frac{2}{3} + x, -\frac{1}{3} + y, -\frac{1}{3} + z$ ; (xiv)  $\frac{1}{3} - x, \frac{2}{3} - y, \frac{1}{3} - z$ ; (xv)  $\frac{1}{3} - x, -\frac{1}{3} - y, \frac{2}{3} - z$ ; (xvi)  $-\frac{2}{3} - x, -\frac{1}{3} - y, \frac{2}{3} - z$ ; (xvii)  $\frac{2}{3} + x, \frac{1}{3} + y, \frac{1}{3} + z$ ; (xviii)  $-\frac{1}{3} + x, \frac{1}{3} + y, \frac{1}{3} + z$ ; (xix)  $-\frac{2}{3} + x, -\frac{2}{3} - y, \frac{1}{3} + z$ .

[6(c)]. Samples of composition  $\text{FeCrGaSe}_4$  could nevertheless possess a non-centrosymmetric  $\text{ZnIn}_2\text{S}_4$ - (IIIa) structure with an ordered cation distribution. A similar centrosymmetric polytype of the  $\text{ZnIn}_2\text{S}_4$ - (IIIa) structure has been reported very recently for layered  $\text{MnIn}_2\text{Se}_4$  (Range, Klement, Döll, Bucher & Baumann, 1991). However, whereas the stacking of the Se layers in  $\text{MnIn}_2\text{Se}_4$  is  $(hM'cM^o cM'h)_3$ , as is common in the case of layered chalcogenides, that of the selenide under study is  $(cM'hM^o hM'c)_3$ . The reason for this unusual stacking, which does not enable a 4 + 1 coordination of the tetrahedrally coordinated metal atoms, is not yet known. The similar  $\text{FeGa}_2\text{S}_4$  structure type is  $(hM'hM^o hM'h)_1$

with sole hexagonal stacking and only one sandwich in the unit cell.

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## Structure of Lithium Copper Pyrophosphate

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**Abstract.**  $\text{Li}_2\text{CuP}_2\text{O}_7$ ,  $M_r = 251.37$ , monoclinic,  $I2/a$ ,  $a = 14.068$  (2),  $b = 4.8600$  (8),  $c = 8.604$  (1) Å,  $\beta = 98.97$  (1)°,  $V = 581.1$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.873$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 4.2911$  mm<sup>-1</sup>,  $F(000) = 484$ ,  $T = 295$  (1) K,  $R = 0.048$  for 414 observed reflections [ $I > 2\sigma(I)$ ]. The pyrophosphate anion is known to adopt varied conformations in different environments. In the present structure analysis, the bridge P—O—P angle is 121.5 (5)°, the P—O(bridge) bond length is 1.618 (4) Å and the P—O(terminal) bond lengths vary between 1.483 (5) and 1.530 (5) Å. The Cu and Li cations are tetracoordinated with Cu—O distances ranging from 1.923 (5) to 1.926 (5) Å and Li—O distances ranging from 1.87 (1) to 1.94 (1) Å.

**Introduction.** Few investigations of the structure of double pyrophosphate compounds of the type  $M_2^I M^{II} P_2 O_7$  are reported in the literature. Complete structural data exist only for  $\text{K}_2\text{CdP}_2\text{O}_7$  (Faggiani & Calvo, 1976) and  $\text{Na}_2\text{CaP}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  ( $\alpha$  and  $\beta$ ) (Cheng, Pritzker & Nyburg, 1980). The title com-

pound,  $\text{Li}_2\text{CuP}_2\text{O}_7$ , was first analysed by powder X-ray diffraction and the pattern was indexed in a monoclinic unit cell with the following dimensions:  $a = 14.050$  (2),  $b = 4.868$  (1),  $c = 8.608$  (2) Å,  $\beta = 98.84$  (2)°. Its complete structure analysis, by single-crystal X-ray diffraction, is presented here.

**Experimental.** To obtain single crystals of  $\text{Li}_2\text{CuP}_2\text{O}_7$ , a stoichiometric mixture of  $\text{Li}_2\text{CO}_3$ ,  $\text{CuCO}_3$ ,  $\text{Cu}(\text{OH})_2$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  was progressively heated to about 1038 K in a platinum crucible; the mixture must be partly fused. After 4 h at this temperature, the mixture was cooled to 873 K and the furnace switched off. The sample was treated with hot water to isolate the crystals. The blue crystals are made up of parallel layers that cleave easily. This made the selection of single crystals suitable for X-ray analysis very difficult, the chosen samples often being twinned. The specimen finally selected was of approximate dimensions  $0.2 \times 0.2 \times 0.05$  mm. X-ray diffraction data were measured with an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation using  $\theta$ - $2\theta$  scans. The unit-cell dimensions were redetermined from 25

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