As shown in Table 2, the In—F distances vary from 2.014 to 2.123 Å with ⟨In—F⟩ = 2.082 Å. In contrast, a wider range of bond lengths is observed for the LiF_6 octahedra owing to weaker bonds (the Li—F distances are between 1.949 and 2.109 Å, ⟨Li—F⟩ = 2.008 Å). Nevertheless, the angular dispersion is larger in the InF_6 ($\Delta = 19°$) than in the LiF_6 octahedra ($\Delta = 13.5°$).

This framework is a new structural type in the AMF_4 family (Babel & Tressaud, 1985). A recent report has pointed out a relationship between the $LiCoF_4$- and $NaCoF_4$-type structures (Lacorre, Pannetier, Averdunk, Hoppe & Ferey, 1989). Similarities have been found either with the rutile-type structure or with perovskite-type layers, thus leading to two possible descriptions for $LiCoF_4$: (*a*) a dirutile-type structure consisting of an alternation of edge-sharing $(CoF_6)^{3-}$ and $(LiF_6)^{5-}$ octahedra along the [101] direction of the monoclinic cell; or (*b*) $(CoF_4)_n^{n-}$ perovskite-type sheets of tilted corner-sharing octahedra, between which Li^+ ions are inserted. For $LiInF_4$: (*a*) the $(InF_4)_n^{n-}$ layers can be idealized as rutile-type sheets with free edges alternatively up and down ($a_R = a$, $b_R = c$); and (*b*) the $(LiF_4)_n^{3n-}$ chains represent a zigzag staking of LiF_6 octahedra similar to that found in the α-PbO_2-type structure.

References

Babel, D. & Tressaud, A. (1985). *Inorganic Fluorides*, edited by P. Hagenmuller, pp. 77–203. New York: Academic Press.

Chaminade, J. P., Garcia, A., Pouchard, M., Fouassier, C., Jacquier, B., Perret-Gallix, D. & Gonzalez-Mestres, L. (1990). *J. Cryst. Growth*, **99**, 799–804.

Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

Gonzalez-Mestres, L. & Perret-Gallix, D. (1988). *Ann. Phys.* **3**, 181–186.

Gonzalez-Mestres, L. & Perret-Gallix, D. (1989). In *Neutrinos 88, Boston*. Singapore: World Scientific.

Grannec, J., Champarnaud, J. C. & Portier, J. (1970). *Bull. Soc. Chim. Fr.* **11**, 3862–3864.

Grannec, J. & Ravez, J. (1970). *C. R. Acad. Sci.* **270**, 2059–2061.

Lacorre, P., Pannetier, J., Averdunk, F., Hoppe, R. & Ferey, G. (1989). *J. Solid State Chem.* **79**, 1–11.

Raghavan, R. S. (1976). *Phys. Rev. Lett.* **37**, 259–262.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1992). C**48**, 771–773

Structure of Europium Zirconium Selenide, $EuZrSe_3$

By Arthur Mar and James A. Ibers*

Department of Chemistry and Science and Technology Center for Superconductivity, Northwestern University, Evanston, IL 60208-3113, *USA*

(*Received* 12 *July* 1991; *accepted* 2 *October* 1991)

Abstract. $EuZrSe_3$, $M_r = 480.07$, orthorhombic, *Pnma*, $a = 8.849\ (2)$, $b = 3.937\ (1)$, $c = 14.348\ (5)$ Å, $V = 499.9\ (2)$ Å^3, $Z = 4$, $D_x = 6.38$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0.7093$ Å, $\mu = 359.6$ cm^{-1}, $F(000) = 805$ (including anomalous dispersion), $T = 294$ K, $R(F^2) = 0.096$ for 973 averaged reflections (including those having $F_o^2 < 0$) and $R(F) = 0.037$ for 593 reflections having $F_o^2 > 3\sigma(F_o^2)$. The structure of $EuZrSe_3$ consists of columns of double edge-sharing Zr octahedra. These columns are linked together by Eu bicapped trigonal prisms.

Introduction. The phase Ln_2MQ_5 (Ln = rare earth; M = Zr, Hf; Q = S, Se) exists for most rare earths with the exception of Eu (Cherkasova & Serebrennikov, 1977; Donohue & Jeitschko, 1974; Jeitschko & Donohue, 1975; Kokhno & Serebrennikov, 1977). By virtue of the high stability of its divalent state, Eu forms the phases $EuZrS_3$ and $EuHfS_3$, which adopt a distorted perovskite structure of the $GdFeO_3$ type (Kazarbina, Maksimov & Serebrennikov, 1981; Lelieveld & IJdo, 1980; Serebrennikov, Senova & Cherkasova, 1979). As part of a general program to elucidate new ternary chalcogenides, we report here the structure of a new ternary selenide, $EuZrSe_3$. $EuZrSe_3$ belongs to the NH_4CdCl_3 structure type (Muller & Roy, 1974), a class of compounds ABX_3 that are differentiated primarily by the coordination number of the large A cation, which can vary from CN3 to CN9. In this respect, the intermediate coordination of Eu (CN8) represents a bridge between the two extremes exhibited by this structure type. This relationship is discussed in more detail below.

Experimental. The compound $EuZrSe_3$ resulted from a reaction of elemental powders ground together in an atomic ratio of Eu:Zr:Se = 1:2:5 (Eu, 26 mg,

---

* To whom correspondence should be addressed.

0108-2701/92/050771-03$06.00

0.17 mmol, 99.9%, AESAR; Zr, 31 mg, 0.34 mmol, 99%, AESAR; Se, 68 mg, 0.86 mmol, 99.5%, Aldrich), loaded into an evacuated quartz tube, and heated in a furnace at 1273 K for 8 d. Small short black needle-shaped crystals were obtained, and the presence of all three elements Eu, Zr and Se was confirmed by EDAX (energy-dispersive analysis by X-rays) measurements with a Hitachi S570 scanning electron microscope.

The crystal used for data collection was a thin needle, 0.02 × 0.24 × 0.01 mm on edge, bounded by {100}, {010}, {001}; crystal volume 6.3×10^{-5} mm^3. Unit-cell parameters were determined from a least-squares analysis of 25 reflections in the range $25 < 2\theta < 35°$, automatically centered on a Picker diffractometer operated from a PC (J. C. Huffman, 1990; unpublished work). Intensity data were collected with the θ–2θ technique with a scan range of 0.9° in 2θ below $K\alpha_1$ to 0.9° above $K\alpha_2$ at a scan speed of 2.0° min^{-1}. Background intensities were counted for 10 s at each end of the scan range. Six standard reflections ($\bar{2}1\bar{2}$, $\bar{3}09$, 125, $\bar{2}0\bar{4}$, $10\bar{5}$ and $0\bar{1}5$) monitored at intervals of every 100 reflections showed no significant change during the course of data collection. A total of 6271 reflections, measured to $[(\sin\theta)/\lambda]_{\max} = 0.723$ Å^{-1} with indices in the range $-12 \le h \le 12$, $-5 \le k \le 5$, $-20 \le l \le 20$, were corrected for absorption with the use of the analytical method (de Meulenaer & Tompa, 1965); minimum and maximum transmission factors were 0.416 and 0.654 respectively. The systematic extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) are consistent with the space groups *Pnma* and $Pn2_1a$. The R index for averaging $(\sum|\langle F^2\rangle - F^2|/\sum F^2)$ was 0.180 (973 unique data) in *Pnma* and 0.176 (1723 unique data) in $Pn2_1a$. As there is no strong support for the non-centrosymmetric space group, the space group *Pnma* was chosen. Of the 973 unique reflections, 593 had $F_o^2 > 3\sigma(F_o^2)$.

The initial positions for all atoms were determined by direct methods with the program *SHELXS*86 (Sheldrick, 1985). Scattering factors and anomalous-dispersion terms were taken from the usual sources (Cromer, 1974; Cromer & Waber, 1974). All calculations were performed on a Stardent ST2500 computer with methods and programs standard in this laboratory (Waters & Ibers, 1977). The program *STRUCTURE TIDY* (Gelato & Parthé, 1987) was used to standardize the crystal structure according to rules formulated earlier (Parthé & Gelato, 1984). The final cycle of least-squares refinement on F_o^2 included anisotropic thermal parameters and resulted in values of $R(F_o^2) = 0.096$, $wR(F_o^2) = 0.107$, and $S = 1.07$ (31 variables, 973 observations) with Δ/σ not exceeding 0.05. The weights were taken as $[\sigma^2(\text{counting statistics}) + (0.04F_o^2)^2]^{-1}$. The value for the conventional R index [on F for $F_o^2 > 3\sigma(F_o^2)$] is 0.037 for 593 observations. The final difference electron density map shows no features with a height greater than 1.8% that of an Eu atom ($\Delta\rho_{\max} = 10.2$; $\Delta\rho_{\min} = -11.7$ e Å^{-3}).

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *for* $EuZRSe_3$ *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Wyckoff position	x	y	z	B_{eq}
Eu	4(c)	0.43709 (9)	$\frac{1}{4}$	0.67788 (6)	1.08 (2)
Zr	4(c)	0.17075 (16)	$\frac{1}{4}$	0.44279 (11)	0.83 (3)
Se(1)	4(c)	0.02024 (16)	$\frac{1}{4}$	0.60885 (10)	0.77 (3)
Se(2)	4(c)	0.15885 (15)	$\frac{1}{4}$	0.01390 (11)	0.83 (3)
Se(3)	4(c)	0.29268 (16)	$\frac{1}{4}$	0.28081 (10)	0.87 (3)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *for* $EuZrSe_3$ *with e.s.d.'s in parentheses*

Eu(a)—Se(1d)	3.147 (2)	Zr(a)—Se(3a)	2.562 (2)
Eu(a)—2Se(3c)	3.153 (1)	Zr(a)—2Se(2b)	2.681 (2)
Eu(a)—2Se(2b)	3.183 (2)	Zr(a)—2Se(1c)	2.698 (2)
Eu(a)—2Se(3b)	3.192 (1)	Zr(a)—Se(1a)	2.730 (2)
Eu(a)—Se(2d)	3.380 (2)		
Eu(a)···Se(1a)	3.819 (2)		

Se(1d)—Eu(a)—2Se(3c)	68.90 (4)	Se(3a)—Zr(a)—2Se(2b)	96.22 (6)
Se(1d)—Eu(a)—2Se(2b)	141.36 (3)	Se(3a)—Zr(a)—2Se(1c)	90.84 (6)
Se(1d)—Eu(a)—2Se(3b)	72.49 (4)	Se(3a)—Zr(a)—Se(1a)	175.70 (8)
Se(1d)—Eu(a)—Se(2d)	130.98 (5)	Se(2b)—Zr(a)—Se(2b)	94.47 (7)
Se(3c)—Eu(a)—Se(3c)	77.25 (4)	Se(2b)—Sr(a)—Se(1c)	85.48 (4)
Se(3c)—Eu(a)—Se(2b)	87.43 (4)	Se(2b)—Zr(a)—Se(1c)	172.90 (8)
Se(3c)—Eu(a)—Se(2b)	136.65 (5)	Se(2b)—Zr(a)—Se(1a)	86.69 (6)
Se(3c)—Eu(a)—Se(3b)	90.64 (2)	Se(1c)—Zr(a)—Se(1c)	93.70 (6)
Se(3c)—Eu(a)—Se(3b)	141.35 (3)	Se(1c)—Zr(a)—Se(1a)	86.22 (5)
Se(3c)—Eu(a)—Se(2d)	73.31 (4)		
Se(2b)—Eu(a)—Se(2b)	76.40 (5)		
Se(2b)—Eu(a)—Se(3b)	77.92 (4)		
Se(2b)—Eu(a)—Se(3b)	123.60 (4)		
Se(2b)—Eu(a)—Se(2d)	63.45 (4)		
Se(3b)—Eu(a)—Se(3b)	76.15 (4)		
Se(3b)—Eu(a)—Se(2d)	138.29 (3)		

Symmetry code: (a) $x, \frac{1}{4}, z$; (b) $-x + \frac{1}{2}, \frac{3}{4}, z + \frac{1}{2}$; ($c$) $-x, \frac{3}{4}, -z$; (d) $x + \frac{1}{2}, \frac{1}{4}, -z + \frac{1}{2}$.

Final values of the atomic parameters and equivalent isotropic thermal parameters are listed in Table 1.* Selected interatomic distances and angles are listed in Table 2. Views down the b axis and down the a axis are given in Figs. 1 and 2, respectively.

Discussion. The structure of $EuZrSe_3$ consists of staggered double columns of edge-sharing Zr octahedra linked together by Eu atoms. The Eu atom is eight coordinate, residing in a bicapped trigonal prism with one capping Se atom further away [3.380 (2) Å] than the other seven [3.147 (2) to 3.192 (1) Å]. There exist several sulfides with a related structure: $SnHfS_3$ and $PbHfS_3$ (Wiegers,

---

* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54709 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0540]

Meetsma, Haange & de Boer, 1989), $PbZrS_3$ (Lelieveld & IJdo, 1978), Sn_2S_3 and $PbSnS_3$ (Jumas, Ribes, Philippot & Maurin, 1972; Mootz & Puhl, 1967; Yamaoka & Okai, 1970); as well as the mixed-anion compound $PbSnSeS_2$ (Jumas, Ribes, Philippot & Maurin, 1972). Owing to the presence of their lone pairs, the Pb or Sn atoms in these compounds reside in highly asymmetric sites and are strongly shifted to one side, forming three short bonds to S atoms (CN3). $EuZrSe_3$ presents a *less* distorted version of this structure, the Eu atoms shifting to a fairly regular bicapped trigonal prismatic site (CN8). Alternatively, if the Se(1) atom at 3.819 (2) Å is taken into account, the Eu atom resides in a distorted tricapped trigonal prismatic site. Then $EuZrSe_3$ presents a *more* distorted version of the $LaCrSe_3$ structure, in which nine equally long La—Se bonds (3.07 to 3.25 Å) define a regular tricapped trigonal prism (CN9) (Huy-Dung, Etienne & Laruelle, 1971), as is found in the parent NH_4CdCl_3 structure type (Muller & Roy, 1974).

Although sulfides and selenides are commonly isostructural, $EuZrS_3$ and $EuZrSe_3$ are not. Rather, $EuZrS_3$ (as well as $EuHfS_3$) has a distorted perovskite structure with the Zr (or Hf) octahedra distorted in such a way as to reduce the Eu coordination to a bicapped trigonal prism (Lelieveld & IJdo, 1980). Although they share the same types of coordination polyhedra (Zr octahedra, Eu bicapped trigonal prisms), $EuZrS_3$ and $EuZrSe_3$ form different structures.

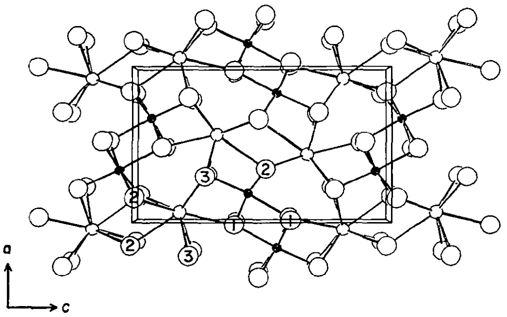

Fig. 1. View of the $EuZrSe_3$ structure down the b axis showing the labeling scheme and unit-cell outline. Here and in Fig. 2 the small solid circles are Zr atoms, the medium open circles are Eu atoms, and the large open circles are Se atoms.

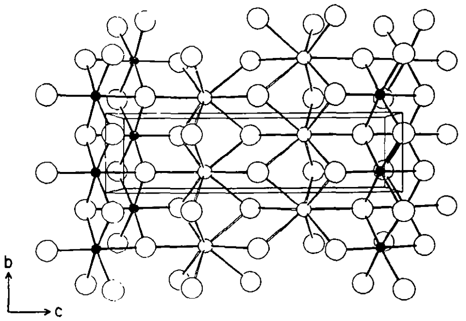

Fig. 2. View of the $EuZrSe_3$ structure down the a axis showing a section at $x = \frac{1}{2}$. Along b the Zr atoms form edge-sharing octahedral chains and the Eu atoms form face-sharing bicapped trigonal prismatic chains.

Preliminary magnetic susceptibility measurements indicate that $EuZrSe_3$ is paramagnetic and obeys the Curie law.

This work was supported by the US National Science Foundation through Grant DMR-88-09854 (Science and Technology Center for Superconductivity) and Grant DMR-88-13623. Use was made of the SEM and magnetic susceptibility facilities of the Materials Research Center at Northwestern University (US National Science Foundation Grant DMR-88-21571).

References

Cherkasova, T. G. & Serebrennikov, V. V. (1977). *Zh. Neorg. Khim.* **22**, 2711–2716.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Donohue, P. C. & Jeitschko, W. (1974). *Mater. Res. Bull.* **9**, 1333–1336.

Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.

Huy-Dung, N., Etienne, J. & Laruelle, P. (1971). *Bull. Soc. Chim. Fr.* pp. 2433–2437.

Jeitschko, W. & Donohue, P. C. (1975). *Acta Cryst.* **B31**, 1890–1895.

Jumas, J.-C., Ribes, M., Philippot, E. & Maurin, M. (1972). *C. R. Acad. Sci. Sér. C*, **275**, 269–272.

Kazarbina, T. V., Maksimov, Yu. M. & Serebrennikov, V. V. (1981). *Zh. Neorg. Khim.* **26**, 1987–1989.

Kokhno, G. V. & Serebrennikov, V. V. (1977). *Zh. Neorg. Khim.* **22**, 2111–2114.

Lelieveld, R. & IJdo, D. J. W. (1978). *Acta Cryst.* **B34**, 3348–3349.

Lelieveld, R. & IJdo, D. J. W. (1980). *Acta Cryst.* **B36**, 2223–2226.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Mootz, D. & Puhl, H. (1967). *Acta Cryst.* **23**, 471–476.

Muller, O. & Roy, R. (1974). *The Major Ternary Structural Families*, pp. 209–210. Berlin: Springer-Verlag.

Parthé, E. & Gelato, L. M. (1984). *Acta Cryst.* **A40**, 169–183.

Serebrennikov, V. V., Senova, R. N. & Cherkasova, T. G. (1979). *Izv. Akad. Nauk SSSR Neorg. Mater.* **15**, 2087–2088.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Waters, J. M. & Ibers, J. A. (1977). *Inorg. Chem.* **16**, 3273–3277.

Wiegers, G. A., Meetsma, A., Haange, R. J. & de Boer, J. L. (1989). *Acta Cryst.* **C45**, 847–849.

Yamaoka, S. & Okai, B. (1970). *Mater. Res. Bull.* **5**, 789–794.