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Single-Crystal Growth and Classification of $EuAlF_5$ and Solid Solutions $M(II)_{1-x}Eu_xAlF_5$ (M = Ca, Sr, Ba) within the Structural Family of Tetragonal $M(II)M(III)F_5$ Compounds

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The compound $EuAlF_5$, as well as the solid solutions $Ca_{0.19(1)}Eu_{0.81(1)}AlF_5$, $Sr_{0.15(1)}Eu_{0.85(1)}AlF_5$, $Sr_{0.55(1)}Eu_{0.45(1)}AlF_5$, $Sr_{0.77(1)}Eu_{0.23(1)}AlF_5$, and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$, crystallize in colorless tetragonal columns. These have been prepared by solid state reactions at 900°C, starting from mixtures of the binary fluorides. According to Vegard's rule the solid solution $Sr_{1-x}Eu_xAlF_5$ shows a linear dependence of the crystal volume on the molar ratio Eu/Sr. All crystal structures have been refined from single-crystal diffractometer data. $EuAlF_5$ and the $M_{1-x}Eu_xAlF_5$ (M = Ca, Sr) compounds obtained are isotypic with β-$SrAlF_5$. They crystallize in a superstructure in space group $I4_1/a$ (no. 88) with 64 formula units and lattice parameters $a \approx 19.9$ Å, $c \approx 14.3$ Å. The structure is characterized by chains of *trans*-corner-sharing $[AlF_{4/2}F_{2/1}]$ and branched $[AlF_{5/1}F_{1/2}]$ octahedra forming a channel structure. Inside the channels isolated ordered dimeric units $[AlF_{4/1}F_{2/2}]_2$ are located. The divalent metal atoms show coordination numbers 8 and 9; they connect the $[AlF_6]$ octahedra into a three-dimensional structure. $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$ is isotypic with the corresponding Sr compound $Ba_{0.43(1)}Sr_{0.57(1)}AlF_5$, and it crystallizes with 16 formula units and lattice parameters $a = 14.3860(7)$ Å, $c = 7.2778(3)$ Å in space group $I4/m$ (no. 87). The network structure is identical with that of $EuAlF_5$. Instead of the dimeric units, infinite chains $[AlF_{4/1}F_{2/2}]_\infty$ of *trans*-corner-sharing $[AlF_6]$ octahedra extending along the c- axis are located inside the channels. The bridging fluorine atoms of this chain show large anisotropic displacement parameters, but no superstructure reflections have been observed for this compound. © 2002 Elsevier Science (USA)

Key Words: **crystal structure; $M(II)M(III)F_5$ structure types; fluorides; Eu(II); solid solutions.**

INTRODUCTION

Complex solid fluorides are interesting compounds for optical hole burning or as host lattices for doping with luminescent rare earth ions (1, 2). They are efficient materials that can be used in a number of optical applications ranging from phosphors to lasers.

The complex divalent aluminium fluorides include representatives with a number of different structure types (3, 4), and for some of these compounds activation of divalent rare earth ions has also been investigated (5–7). One of the most interesting candidates within this structural family is $SrAlF_5$ for which at least two crystalline polymorphs are known, tetragonal β-$SrAlF_5$ (7) and monoclinic α'-$SrAlF_5$ (8). The structure of the tetragonal modification was originally published as crystallizing in space group $I4$ with lattice parameters $a = 14.089(2)$ Å, $c = 7.617(2)$ Å, but some structural discrepancies remained (original citation: "To a first approximation the space group is $I4$, but a small distortion along the c axis in fact doubles the c parameter, the space group becoming $P4$" (9)). Later the structure was redetermined in space group $I4_1/a$ taking into account superstructure reflections along [110] and [001] (in respect of the original cell), which resulted in the fourfold unit cell with lattice parameters $a = 19.8822(14)$ Å, $c = 14.3224(19)$ Å (7).

The corresponding divalent europium phase, $EuAlF_5$, is reported to be isotypic with tetragonal $SrAlF_5$ (10). Powder data of this specimen were indexed on the basis of the old structural parameters of $SrAlF_5$ in $I4$ with $a = 14.12(1)$ Å, $c = 7.185(3)$ Å (10). Recently single-crystal structure analyses of $SmAlF_5$ (11) and $YbAlF_5$ (12) have been published (space group $I4/m$, $a = 14.144(4)$ Å, $c = 7.222(3)$ Å for $SmAlF_5$ and $a = 13.803(3)$ Å, $c = 7.013(3)$ Å for $YbAlF_5$), resulting in a structure where some of the fluorine atoms are disordered. The structures of both divalent rare earth aluminium fluorides are isotypic with $BaTiF_5$ (13). Since the divalent rare earth ions show a closely related crystal chemistry and have ionic radii of 1.30 Å (Eu^{2+}) and 1.32 Å (Sm^{2+}) for CN (coordination number) = 9 similar to 1.31 Å for Sr^{2+} (14),[2] it seemed desirable to redetermine the

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[2] The values for Yb^{2+} with CN = 9 are missing in the original paper (14). Due to the ionic radius being smaller than that of divalent Eu or Sm, Yb^{2+} compounds are more related to the corresponding Ca^{2+} compounds.

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structure of $EuAlF_5$ from single-crystal data and to check whether the Eu(II) compound crystallizes in the β-$SrAlF_5$, the $BaTiF_5$, or the closely related $Ba_{0.43(1)}Sr_{0.57(1)}AlF_5$ (7) structure type.

This article reports on the preparation and single-crystal structure analyses of $EuAlF_5$ and different solid solutions $M_{1-x}Eu_xAlF_5$ with M = Ca, Sr, Ba. A classification of the different $M_{1-x}Eu_xAlF_5$ phases within the crystal chemistry of $M(II)M(III)F_5$ compounds is given, and the relations between the β-$SrAlF_5$, $BaTiF_5$, and $Ba_{0.43(1)}Sr_{0.57(1)}AlF_5$ structure types are briefly discussed.

EXPERIMENTAL

The binary fluorides AlF_3 (Merck, Patinal), CaF_2 (Merck, Suprapur), BaF_2 (Riedel de Haën, pure), SrF_2 (Riedel de Haën, pure), and EuF_2 were used as educts. EuF_2 was prepared by reduction of EuF_3 (Chempur, 99.9%) with H_2 at 1100°C, as described in (15). Before use AlF_3, CaF_2, BaF_2, and SrF_2 were dried at 250°C for 3 h in vacuum (10^{-3} Torr). For preparation of solid solutions $M_{1-x}Eu_xAlF_5$ (M = Ca, Ba) a nominal composition of MF_2:EuF_2:AlF_3 = 1:1:2 ("$M_{0.5}Eu_{0.5}AlF_5$") was applied as the starting mixture. For different phases of the solid solution $Sr_{1-x}Eu_xAlF_5$ stoichiometric ratios of SrF_2:EuF_2:AlF_3 = 1:3:4, 1:1:2 and 3:1:4 according to a nominal composition of $Sr_{0.25}Eu_{0.75}AlF_5$, $Sr_{0.5}Eu_{0.5}AlF_5$, and $Sr_{0.75}Eu_{0.25}AlF_5$ were employed.

For single-crystal growth the binary fluorides were initially mixed in a ball mill, pressed to tablets, and placed in a stainless steel container sheathed with a molybdenum foil to avoid incorporation of iron or other impurities into the structure. Before closing the container approximately 50 mg NH_4HF_2 (Fluka, p.A.) was added to increase the HF pressure, to expel the remaining oxygen, and to adjust a slightly reducing atmosphere during the reaction. The reactors were then heated to 900°C in the course of 20 h, kept at that temperature for 24 h, and then slowly cooled down to 700°C

TABLE 1
Details of Data Collection and Structure Refinement

	Compound					
	$EuAlF_5$	$Ca_{0.19(1)}Eu_{0.81(1)}AlF_5$	$Sr_{0.15(1)}Eu_{0.85(1)}AlF_5$	$Sr_{0.55(1)}Eu_{0.45(1)}AlF_5$	$Sr_{0.77(1)}Eu_{0.23(1)}AlF_5$	$Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$
Diffractometer	Siemens SMART CCD detector					
Radiation; λ(Å)	MoK_α 0.71073					
Temperature (°C)	22(2)					
Crystal dimensions [mm^3]	0.06·0.06·0.09	0.07·0.07·0.25	0.06·0.08·0.10	0.09·0.09·0.31	0.03·0.03·0.10	0.07·0.07·0.28
Crystal description	Colorless tetragonal column					
Space group (no.)	$I4_1/a$ (88), origin choice 2					$I4/m$ (87)
Formula units Z	64					16
a (Å)	19.9642(7)	19.8625(8)	19.9510(6)	19.9203(11)	19.9036(10)	14.3860(7)
c (Å)	14.3731(5)	14.2928(6)	14.3656(5)	14.3445(11)	14.3279(10)	7.2778(3)
V (Å^3)	5728.7(3)	5638.8(4)	5718.1(3)	5692.2(6)	5676.0(6)	1506.19(12)
Formula weight (g·mol^{-1})	273.94	252.77	264.05	238.54	224.23	264.90
μ (mm^{-1})	17.748	15.001	17.402	16.501	15.996	13.100
X-ray density (g·cm^{-3})	5.082	4.764	4.907	4.454	4.198	4.673
Range θ_{min}–θ_{max}	1.75–30.00	1.76–29.99	1.75–30.00	1.75–30.00	1.75–30.04	2.00–30.00
Range h	$-27 \rightarrow 28$	$-27 \rightarrow 27$	$-27 \rightarrow 28$	$-28 \rightarrow 27$	$-27 \rightarrow 27$	$-20 \rightarrow 20$
k	$-27 \rightarrow 28$	$-27 \rightarrow 27$	$-28 \rightarrow 26$	$-27 \rightarrow 27$	$-27 \rightarrow 27$	$-20 \rightarrow 20$
l	$-19 \rightarrow 20$	$-20 \rightarrow 20$	$-18 \rightarrow 19$	$-20 \rightarrow 20$	$-19 \rightarrow 20$	$-10 \rightarrow 10$
Absorption correction	SADABS (16)					
Structure refinement	SHELX97 (17)					
Measured reflections	41160	40204	29999	40013	30602	10537
Independent reflections	4178	4099	4144	4149	4140	1169
Obs. reflections [$I > 2\sigma(I)$]	2137	2599	2108	2787	2161	1154
R_i	0.043	0.037	0.037	0.042	0.050	0.030
Trans. coef. T_{min}; T_{max}	0.6957; 1.0000	0.6005; 1.0000	0.5538; 1.0000	0.4573; 1.0000	0.4312; 1.0000	0.5422; 1.0000
Number of parameters	255	259	259	259	259	80
Ext. coef. (SHELXL97)	0.000366(6)	0.000083(4)	0.000207(4)	0.000701(12)	0.000390(12)	0.00219(11)
Diff. elec. dens. max; min (e$^-$·Å^{-3}) (dist. (Å), atom)	1.13 (0.79, Eu1) −0.95 (1.69, F17)	1.48 (0.87, Ca1) −0.89 (1.74, F6)	1.09 (0.74, Sr2) −0.88 (0.71, Sr4)	1.59 (0.73, Sr1) −0.84 (0.86, Sr3)	0.92 (0.62, Sr2) −0.62 (0.80, Sr4)	2.06 (0.63, Ba1) −1.55 (0.64, Ba1)
$R[F^2 > 2\sigma(F^2)]$	0.0213	0.0212	0.0203	0.0242	0.0245	0.0242
$wR2(F^2$ all)	0.0585	0.0639	0.0563	0.0668	0.0699	0.0599
Goof	0.972	1.128	0.909	1.186	0.926	1.266
CSD number	412020	412021	412022	412023	412024	412025

at a cooling rate of 4°C$\cdot$h^{-1}, kept again at 700°C for 24 h, and cooled down to room temperature overnight.

For all of the batches, columnar translucent single crystals with tetragonal habit and a length of up to 0.5 mm could be isolated from the reaction products. Before X-ray data collection the single crystals were checked under a polarizing microscope. All crystals were found to be of good optical quality and showed uniaxial behavior in accordance with the tetragonal crystal system. EDX analyses of selected crystals showed no elements present other than those

TABLE 2
$EuAlF_5$ and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	Wyckoff position	x	y	z	U_{eq}	s.o.f.
			$EuAlF_5$			
Eu1	16*f*	0.080170(12)	0.113688(12)	0.62779(3)	0.01084(7)	1
Eu2	16*f*	0.081372(12)	0.115213(12)	0.12092(3)	0.01054(7)	1
Eu3	16*f*	0.160705(12)	0.158079(12)	0.37491(3)	0.01188(7)	1
Eu4	16*f*	0.409824(12)	0.090484(12)	0.12411(3)	0.01111(7)	1
Al1	16*f*	0.07738(7)	0.00778(7)	0.37444(17)	0.0084(3)	1
Al2	16*f*	0.25144(7)	0.00149(7)	0.1243(2)	0.0081(2)	1
Al3	16*f*	0.25678(7)	0.17603(7)	0.12564(17)	0.0085(3)	1
Al4	8*e*	0	1/4	0.27048(12)	0.0097(4)	1
Al5	8*e*	0	1/4	0.48065(12)	0.0087(4)	1
F1	16*f*	0.01026(14)	0.00556(15)	0.6232(3)	0.0164(6)	1
F2	16*f*	0.01339(13)	0.00883(15)	0.1261(3)	0.0164(6)	1
F3	16*f*	0.03227(17)	0.33187(17)	0.2679(2)	0.0168(7)	1
F4	16*f*	0.05430(13)	0.22863(14)	0.3756(2)	0.0127(5)	1
F5	16*f*	0.06754(17)	0.22668(16)	0.5551(2)	0.0150(7)	1
F6	16*f*	0.06728(17)	0.22642(16)	0.1957(2)	0.0146(7)	1
F7	16*f*	0.0733(3)	0.0741(3)	0.2879(3)	0.0161(11)	1
F8	16*f*	0.0753(3)	0.0735(3)	0.4606(3)	0.0166(11)	1
F9	16*f*	0.16127(14)	0.01942(13)	0.6253(4)	0.0152(6)	1
F10	16*f*	0.16384(14)	0.02206(14)	0.1274(4)	0.0149(6)	1
F11	16*f*	0.16743(13)	0.02583(14)	0.3723(4)	0.0154(6)	1
F12	16*f*	0.1935(2)	0.1610(3)	0.2111(3)	0.0166(12)	1
F13	16*f*	0.1927(2)	0.1575(3)	0.0403(3)	0.0149(11)	1
F14	16*f*	0.1919(2)	0.1598(3)	0.5376(3)	0.0162(12)	1
F15	16*f*	0.25120(17)	0.00304(16)	0.0012(4)	0.0219(6)	1
F16	16*f*	0.27819(14)	0.08657(14)	0.1286(4)	0.0152(6)	1
F17	16*f*	0.3231(2)	0.1823(3)	0.0392(3)	0.0169(11)	1
F18	16*f*	0.3221(3)	0.1838(3)	0.2104(3)	0.0210(12)	1
F19	16*f*	0.4063(3)	0.5555(2)	0.0423(3)	0.0157(12)	1
F20	16*f*	0.46847(17)	0.16772(17)	0.0165(2)	0.0164(7)	1
			$Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$			
Eu1	8*h*	0.07083(2)	0.24472(2)	0	0.01800(13)	0.39(3)
Ba1	8*h*	0.07083(2)	0.24472(2)	0	0.01800(13)	0.61(3)
Eu2	8*h*	0.28022(2)	0.44419(2)	0	0.01436(12)	0.38(3)
Ba2	8*h*	0.28022(2)	0.44419(2)	0	0.01436(12)	0.62(3)
Al1	8*h*	0.32056(10)	0.16518(11)	0	0.0115(4)	1
Al2	4*e*	0	0	0.2458(3)	0.0115(4)	1
Al3	4*e*	0	1/2	0	0.0097(4)	1
F1	16*i*	0.10219(17)	0.28808(17)	0.3307(3)	0.0219(5)	1
F2	16*i*	0.11347(19)	− 0.0450(2)	0.2574(7)	0.0457(10)	1
F3	16*i*	0.24911(18)	0.10687(19)	0.1683(4)	0.0250(6)	1
F4	8*h*	0.1055(2)	0.4336(2)	0	0.0173(7)	1
F5	8*h*	0.2481(3)	0.2656(3)	0	0.0290(9)	1
F6	8*h*	0.3895(2)	0.0570(2)	0	0.0179(7)	1
F7	4*d*	0	1/2	1/4	0.0203(9)	1
F8	2*b*	0	0	1/4	0.094(6)	1
F9	2*a*	0	0	0	0.102(6)	1

Note. $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ (Å^2).

expected. X-ray data were collected on a Siemens SMART diffractometer equipped with a CCD camera. All intensity data were corrected for Lorentz and polarization effects, and absorption corrections using the multiscan technique (16) were applied. Structure solution and refinement were performed with the SHELX97 program package (17). The x values of the solid solutions $M_{1-x}Eu_xAlF_5$ (M = Ca, Ba) and $Sr_{1-x}Eu_xAlF_5$ were determined by refinement of the site occupation factors (s.o.f.) of the divalent metal positions. This led to a composition of $Ca_{0.19(1)}Eu_{0.81(1)}AlF_5$ and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$ for the respective Ca- and Ba-containing phases, and $Sr_{0.15(1)}Eu_{0.85(1)}AlF_5$, $Sr_{0.55(1)}Eu_{0.45(1)}AlF_5$, and $Sr_{0.77(1)}Eu_{0.23(1)}AlF_5$ for phases of the solid solution $Sr_{1-x}Eu_xAlF_5$.

Details of data collection and structure refinements for all structures are given in Table 1. Atomic parameters and selected interatomic distances for $EuAlF_5$ and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$ are listed in Tables 2 and 3, respectively. Owing to limited space and the nearly identical atomic parameters and distances to those in $EuAlF_5$, no particular information for the other solid solutions $M_{1-x}Eu_xAlF_5$ (M = Ca, Sr) are listed. Detailed data on these structures as well as additional crystallographic information on $EuAlF_5$ and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$ can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Karlsruhe-Leopoldshafen, Germany, e-mail: crysdata@FIZ-Karlsruhe.de, quoting the literature citation and the depository CSD numbers for each compound, which are listed at the end of Table 1.

RESULTS AND DISCUSSION

Although many different structure types for complex fluorides with the formula $M(II)M(III)F_5$ are known (3, 4), common building units of all these structures are corner linked $[M(III)F_{4/1}F_{2/2}]$ octahedra. Depending on the size of the M(II) ion and the adopted structure type, the CN could range from 7 to 13 for alkaline earth or divalent rare earth ions within these compounds. For structures crystallizing in tetragonal body-centred space groups, three closely related

TABLE 3
$EuAlF_5$ and $Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$: Selected Interatomic Distances (Å)

			$EuAlF_5$				
Eu1		**Eu2**		**Eu3**		**Eu4**	
–F17	2.470(4)	–F18	2.481(4)	–F14	2.420(4)	–F20	2.478(3)
–F9	2.483(3)	–F6	2.483(3)	–F12	2.445(4)	–F13	2.479(4)
–F5	2.499(3)	–F10	2.486(3)	–F2	2.509(3)	–F3	2.479(3)
–F8	2.536(4)	–F2	2.522(3)	–F4	2.549(3)	–F19	2.492(4)
–F1	2.571(3)	–F7	2.542(4)	–F11	2.644(3)	–F1	2.495(3)
–F5	2.662(3)	–F13	2.645(5)	–F10	2.647(3)	–F9	2.613(3)
–F19	2.693(5)	-F6	2.669(3)	–F8	2.697(5)	–F16	2.630(3)
–F14	2.739(5)	–F12	2.744(5)	–F7	2.724(5)	–F17	2.800(5)
–F20	2.890(3)	–F3	2.859(3)	mean	〈2.580〉	–F18	2.842(5)
mean	〈2.615〉	mean	〈2.603〉			mean	〈2.590〉
Al1		**Al2**		**Al3**		**Al4**	
–F1	1.770(3)	–F11	1.765(3)	–F2	1.772(3)	–F3 ×2	1.757(3)
–F19	1.771(5)	–F15	1.771(6)	–F12	1.787(5)	–F6 ×2	1.783(3)
–F8	1.805(5)	–F16	1.782(3)	–F18	1.791(5)	–F4 ×2	1.908(3)
–F7	1.818(5)	–F9	1.792(3)	–F13	1.811(5)	mean	〈1.816〉
–F14	1.831(5)	–F10	1.797(3)	–F17	1.820(5)	**Al5**	
–F11	1.834(3)	–F15	1.824(6)	–F16	1.837(3)	–F20 ×2	1.760(3)
mean	〈1.805〉	mean	〈1.789〉	mean	〈1.803〉	–F5 ×2	1.783(3)
						–F4 ×2	1.907(3)
						mean	〈1.817〉
			$Ba_{0.62(1)}Eu_{0.38(1)}AlF_5$				
Ba1/Eu1		**Ba2/Eu2**		**Al1**		**Al2**	
–F1 ×2	2.527(2)	–F4	2.519(3)	–F5	1.782(4)	–F2 ×4	1.758(3)
–F5	2.567(5)	–F3 ×2	2.558(3)	–F1 ×2	1.791(3)	–F9	1.789(2)
–F2 ×2	2.686(4)	–F5	2.610(4)	–F3 ×2	1.806(3)	–F8	1.850(2)
–F4	2.763(3)	–F2 ×2	2.750(4)	–F6	1.846(3)	mean	〈1.799〉
–F6	2.779(3)	–F1 ×2	2.766(3)	mean	〈1.804〉	Al3	
–F3 ×2	2.835(3)	mean	〈2.660〉			–F6 ×2	1.789(3)
mean	〈2.689〉					–F4 ×2	1.793(3)
						–F7 ×2	1.8195
						mean	〈1.801〉

structure types are known: The β-SrAlF$_5$ superstructure type (7) (space group $I4_1/a$), the BaTiF$_5$ type (13) ($I4/m$), and Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$-like structures (7) ($I4/m$). The transformation matrix describing the relation between the β-SrAlF$_5$ type and the two others is given as

BaTiF$_5$ or Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$ to β-SrAlF$_5$:

$$(a \approx 14.1\ \text{Å},\ c \approx 7.1\ \text{Å})\ (a \approx 19.9\ \text{Å},\ c \approx 14.2\ \text{Å})$$

$$\boldsymbol{P} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}; \quad \det(\boldsymbol{P}) = 4.$$

All three structures types are characterized by chains of *trans*-corner-sharing $[M(\text{III})\text{F}_{4/2}\text{F}_{2/1}]$ and branched $[M(\text{III})\text{F}_{5/1}\text{F}_{1/2}]$ octahedra, thus forming an assembly with channels propagating along the c axis. The unique building blocks for each structure type are located inside the channels (Figs. 1 and 2). In β-SrAlF$_5$-like structures ordered dimeric units $[M(\text{III})\text{F}_{4/1}\text{F}_{2/2}]_2$ built of two edge-sharing $[M(\text{III})\text{F}_6]$ octahedra are found, whereas in BaTiF$_5$-like structures these dimeric units are disordered and the corresponding fluorine atom sites are half-occupied. The geometry around each M(III) in the dimeric unit is highly distorted from an ideal octahedral arrangement. The bridging fluorine atoms F$_b$ (F4 in EuAlF$_5$) show longer distances to the metal atoms and the angles $\angle(\text{F}_b\text{–}M(\text{III})\text{–F}_b)$ are considerably compressed (approx. 75°), whereas the angles $\angle(M(\text{III})\text{–F}_b\text{–}M(\text{III}))$ are more opened (approx. 105°). Distances $d(M(\text{III})\text{–}M(\text{III}))$ of ≈ 3 Å within a dimer are comparatively short, whereas the separation of two metal atoms belonging to different dimers (≈ 4.2 Å) is substantially larger. Figure 2 demonstrates that the ordering of these dimeric units is the reason for the superstructure arrangement. The main difference between the first two structure types with dimeric units and the Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$-like structures is found in the variation of the $[M(\text{III})\text{F}_6]$ arrangement inside the channel. Here infinite $[\text{AlF}_{4/1}\text{F}_{2/2}]_\infty$ chains of *trans*-corner-sharing [AlF$_6$] octahedra are observed. The bridging fluorine atoms of this chain display large anisotropic displacement parameters. Determining whether this phenomenon is caused by a statistical or a dynamical disorder is the subject of our current research. However, no superstructure reflections have been found for this structure. Compared to the dimeric units the metal-metal separation within a chain is ≈ 3.6 and 3.7 Å. Since the lattice parameters c of all three structure types are comparable (taking into account that in β-SrAlF$_5$ structures the c axis is doubled) the average metal-metal distance is nearly the same.

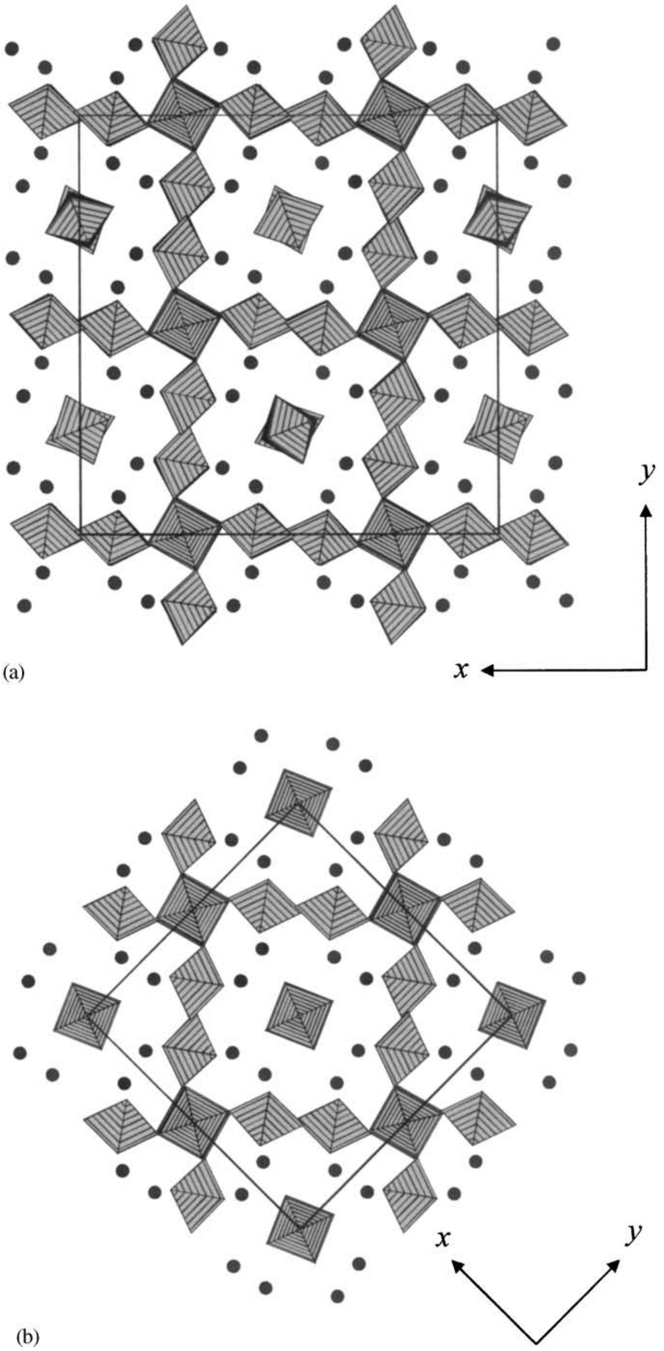

FIG. 1. Projection of the structure along [001] for (a) the β-SrAlF$_5$ structure type and (b) the Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$ structure type. $[M(\text{III})\text{F}_6]$ groups are depicted as hatched octahedra, divalent metal atoms as black spheres. The network of the BaTiF$_5$ structure type is identical to that of Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$.

EuAlF$_5$ and the solid solutions Ca$_{0.19(1)}$Eu$_{0.81(1)}$AlF$_5$, Sr$_{0.15(1)}$Eu$_{0.85(1)}$AlF$_5$, Sr$_{0.55(1)}$Eu$_{0.45(1)}$AlF$_5$, and Sr$_{0.77(1)}$Eu$_{0.23(1)}$AlF$_5$ adopt the β-SrAlF$_5$ structure type, whereas Ba$_{0.62(1)}$Eu$_{0.38(1)}$AlF$_5$ crystallizes isotypically with Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$. Incorporation of the larger Ba^{2+} ions into the Sr^{2+} or Eu^{2+} structure obviously stabilizes this kind of arrangement. If a coordination of fluorine atoms is considered for distances < 3 Å, in EuAlF$_5$ and related solid

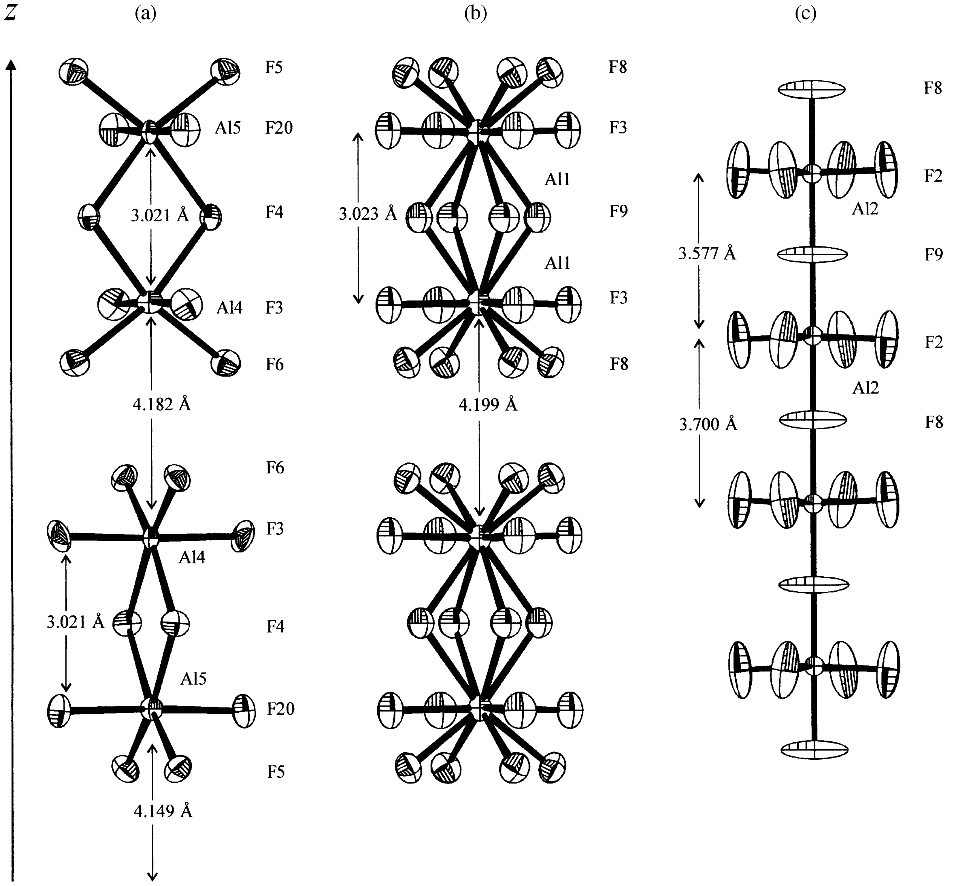

FIG. 2. ORTEP (19) plot of the different arrangements of [AlF$_6$] octahedra located inside the channels with thermal ellipsoids drawn at the 75% probability level. (a) EuAlF$_5$ with ordered dimers (β-SrAlF$_5$ structure type); (b) SmAlF$_5$ (structural data from (11)) with disordered dimers (BaTiF$_5$ structure type); (c) Ba$_{0.62(1)}$Eu$_{0.38(1)}$AlF$_5$ with *trans*-[AlF$_{4/1}$F$_{2/2}$]$_\infty$ chains (Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$ structure type). For all three structure types Al–Al distances are denoted.

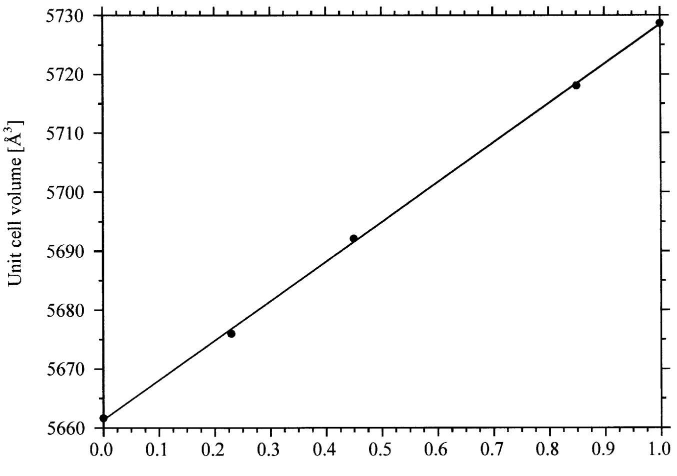

FIG. 3. Sr$_{1-x}$Eu$_x$AlF$_5$. Unit cell volume (Å^3) as a function of the mole fraction x. The size of the points corresponds approximately to the threefold standard deviation for the unit cell volume and the single standard deviation for the mole fraction, respectively.

solutions M_{1-x}Eu$_x$AlF$_5$ (M = Ca, Sr), metal atoms (Eu/M)1, (Eu/M)2 have CN = 9 and (Eu/M)3, (Eu/M)4 have CN = 8. In Ba$_{0.62(1)}$Eu$_{0.38(1)}$AlF$_5$ metal atoms (Eu/Ba)1 and (Eu/Ba)2 have CN = 8. For both structure types the mean Al–F distance of the different [AlF$_6$] octahedra is comparable and is in a typical range for other fluoroaluminates (Table 3).

The Sr$_{1-x}$Eu$_x$AlF$_5$ solid solution shows a linear dependence of the crystal volume on the molar ratio Eu / Sr, which is in accordance with Vegard's rule (18) (Fig. 3). This, and the fact that the compounds Ca$_{0.33(1)}$Sr$_{0.67(1)}$AlF$_5$ (8) and Ba$_{0.43(1)}$Sr$_{0.57(1)}$AlF$_5$ (7) are isotypic with the corresponding Eu(II) compounds, is evidence for the close relationship between the crystal chemistry of Eu^{2+} and Sr^{2+}.

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