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$Eu_3F_4S_2$: Synthesis, crystal structure, and magnetic properties of the mixed-valent europium(II,III) fluoride sulfide $EuF_2 \cdot (EuFS)_2$

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ABSTRACT

Using the method to synthesize rare-earth metal(III) fluoride sulfides *MFS* (*M*=Y, La, Ce–Lu), in some cases we were able to obtain mixed-valent compounds such as $Yb_3F_4S_2$ instead. With $Eu_3F_4S_2$ another isotypic representative has now been synthesized. $Eu_3F_4S_2$ (tetragonal, *I*4/*mmm*, a=400.34(2), c=1928.17(9) pm, Z=2) is obtained from the reaction of metallic europium, elemental sulfur, and europium trifluoride in a molar ratio of 5:6:4 within seven days at 850 °C in silica-jacketed gas-tightly sealed platinum ampoules. The single-phase product consists of black plate-shaped single crystals with a square cross section, which can be obtained from a flux using equimolar amounts of NaCl as fluxing agent. The crystal structure is best described as an intergrowth structure, in which one layer of CaF_2-type EuF_2 is followed by two layers of PbFCl-type EuFS when sheeted parallel to the (001) plane. Accordingly there are two chemically and crystallographically different europium cations present. One of them (Eu^{2+}) is coordinated by eight fluoride anions in a cubic fashion, the other one (Eu^{3+}) exhibits a monocapped square antiprismatic coordination sphere with four F^- and five S^{2-} anions. Although the structural ordering of the different charged europium cations is plausible, a certain amount of charge delocalization with some polaron activity has to take place, which is suggested by the black color of the title compound. Temperature dependent magnetic susceptibility measurements of $Eu_3F_4S_2$ show Curie–Weiss behavior with an experimental magnetic moment of 8.19(5) μ_B per formula unit and a paramagnetic Curie temperature of 0.3(2) K. No magnetic ordering is observed down to 4.2 K. In accordance with an ionic formula splitting like $(Eu^{II})(Eu^{III})_2F_4S_2$ only one third of the europium centers in $Eu_3F_4S_2$ carry permanent magnetic moments. ^{151}Eu-Mössbauer spectroscopic experiments at 4.2 K show one signal at an isomer shift of −12.4(1) mm/s and a second one at 0.42(4) mm/s. These signals occur in a ratio of 1:2 and correspond to Eu^{2+} and Eu^{3+}, respectively. The spectra at 78 and 298 K are similar, thus no change in the Eu^{2+}/Eu^{3+} fraction can be detected.

1. Introduction

The quest for energy efficient materials in all parts of daily life is a major challenge nowadays. Considering luminescent materials, different topics are subject to intense research [1,2]. In the case of coating materials for imaging plates the focus hits PbFCl-type compounds (e.g. BaFCl:Eu^{2+} as imaging plate material for X-ray diffraction [3]), therefore our interest lies in the synthesis and investigation of related materials. Recently we have reported a simple and rapid synthesis technique to obtain pure and crystalline rare-earth metal(III) fluoride sulfides (*MFS*; *M*=Y, La–Lu) [4–8]. Furthermore, we were able to show that ytterbium forms two different compounds, YbFS [5] with trivalent ytterbium and mixed-valent $Yb_3F_4S_2$ [9] containing Yb^{2+} and Yb^{3+} cations, subject to the actual reaction conditions. The latter was synthesized phase-pure by the same technique with appropriate ratios of the applied educts (YbF_3, Yb, and S). With $Eu_3F_4S_2$ [10], we were now able to obtain a compound with the same mixed-valent composition as in the ytterbium system. The determination of the crystal structure by X-ray single-crystal diffraction shows that both compounds are isotypic. $Yb_3F_4S_2$ and $Eu_3F_4S_2$ form black crystals. These observations motivated investigations on the magnetic and charge-ordering properties of the mixed-valent europium(II,III) fluoride sulfide.

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2. Experimental

2.1. Synthesis

$Eu_3F_4S_2$ is formed by the reaction of elemental europium (99.9%, ChemPur, Karlsruhe, Germany) with sulfur (99.999% ChemPur, Karlsruhe, Germany) and europium trifluoride (99.99%, ChemPur, Karlsruhe, Germany) with a molar ratio of 5:6:4 (850 °C, 7*d*) in silica-jacketed gas-tightly sealed platinum capsules using an equimolar quantity of NaCl (E. Merck; suprapur) as fluxing agent. Rinsing the product with demineralized water leads to phase-pure samples of $Eu_3F_4S_2$, which are resistant to air and moisture. Black $Eu_3F_4S_2$ forms thin plate-shaped single crystals with a square habit.

2.2. X-ray Crystallography

Single-crystal X-ray diffraction data have been collected on a STOE IPDS I diffractometer using graphite-monochromatized Mo-*K*α radiation (λ=71.073 pm). The crystallographic data and details of the data collection are listed in Table 1 [11–13].

Table 1
Crystallographic data for $Eu_3F_4S_2$.

Crystal system, space group	Tetragonal, *I*4/*mmm* (no. 139)
Formula units, *Z*	2
Lattice parameters,	
a (pm)	400.34(2)
c (pm)	1928.17(9)
c/*a* ratio	4.816
Calculated density, D_x (g/cm^3)	6.41
Molar volume, V_m (cm^3/mol)	93.05
F(000)	514
Index range, $\pm h/\pm k/\pm l$	6/6/28
θ range, θ_{min}–θ_{max}	4.2–32.8
Absorption coefficient, μ (mm^{-1})	30.7
Data corrections	Background, polarization and Lorentz factors; numerical absorption correction by the program *HABITUS* [11]
Reflections, collected/unique	2243/214
R_{int}/R_σ	0.027/0.010
Structure solution and refinement	Program package *SHELX*-97 [12]
Scattering factors	According to *International Tables, Vol. C* [13]
R_1 for reflections with $\lvert F_o\rvert \geq 4\sigma(F_o)$	0.023 (189)
R_1/wR_2 for all reflections	0.026/0.045
Goodness of fit (GooF)	1.295
Extinction, *g*	0.021(1)
Residual electron density, ρ / e$^-\cdot 10^{-6}$ pm^{-3}, min/max	−1.63/2.22

Table 2 shows the positional parameters, coefficients of the displacement parameters and selected interatomic distances. Further details of the crystal structure investigation are available from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-420637.

2.3. Magnetic Measurements

The magnetic susceptibilities of a polycrystalline, powdered sample of $Eu_3F_4S_2$ were determined with a MPMS *XL* SQUID magnetometer (Quantum Design) in a temperature range of 4.2–300 K with magnetic flux densities up to 5 T. A quantity of 14.66 mg was enclosed in a small silica tube and fixed on the sample holder rod. The sample was then cooled to 4.2 K in zero magnetic field and slowly heated to room temperature in an applied external field.

2.4. Mössbauer Spectroscopy

The 21.53 keV transition of ^{151}Eu with an activity of 130 MBq (2% of the total activity of a ^{151}Sm:EuF_3 source) was used for the Mössbauer spectroscopic investigations. The measurements were carried out with a helium bath cryostat. The temperature of the absorber could be varied from 4.2 to 300 K and was measured with a metallic resistance thermometer with accuracy better than ±0.5 K. The source was kept at room temperature. The sample was placed within a PVC container at a thickness corresponding to about 10 mg Eu/cm^2.

3. Results and Discussion

3.1. Crystal Structure

The title compound crystallizes tetragonally in space group *I*4/*mmm* (*a*=400.34(2) and *c*=1928.17(9) pm) with two formula units per unit cell. The structure of $Eu_3F_4S_2$ is isotypic to $Yb_3F_4S_2$ [9], and can thus be described as an ordered intergrowth-structure according to $EuF_2\cdot(EuFS)_2$ (Fig. 1) consisting of one CaF_2-analogous sheet and two PbFCl-type layers. The existence of the border phases (EuF_2 [14,15]: CaF_2 type [16]; A-EuFS [4,5,17–19]: PbFCl type [20]) confirms this formulation. In the crystal structure there are two crystallographically different europium cations. Eu1 is coordinated by eight F^- anions in the shape of a tetragonal prism. Two additional S^{2-} anions above and below the square F^- planes (Fig. 2, *left*) complete the coordination number to *CN*=8+2. The coordination polyhedron around Eu2 can be compared with that for Eu in A-EuFS [5] where four F^- anions and

Table 2
Atomic coordinates, anisotropic displacement parameters (U_{ij}/pm, U_{12}=U_{13}=U_{23}=0), and selected interatomic distances (*d*/pm) for $Eu_3F_4S_2$.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	U_{11}	U_{22}	U_{33}
Eu1	2*a*	0	0	0	84(3)	$=U_{11}$	101(4)
Eu2	4*e*	0	0	0.33884(3)	97(3)	$=U_{11}$	92(4)
F	8*g*	0	1/2	0.4185(3)	162(30)	239(34)	188(24)
S	4*e*	0	0	0.1895(2)	125(9)	$=U_{11}$	150(13)

Eu1–F	254.5	(8 ×)	F–Eu1	254.5	(2 ×)
Eu1–S	365.4	(2 ×)	F–Eu2	252.3	(2 ×)
Eu2–F	252.3	(4 ×)	S–Eu2	288.0	(1 ×)
Eu2–S	288.0	(1 ×)	S–Eu2′	288.3	(4 ×)
Eu2–S′	288.3	(4 ×)	S–Eu1	365.4	(1 ×)

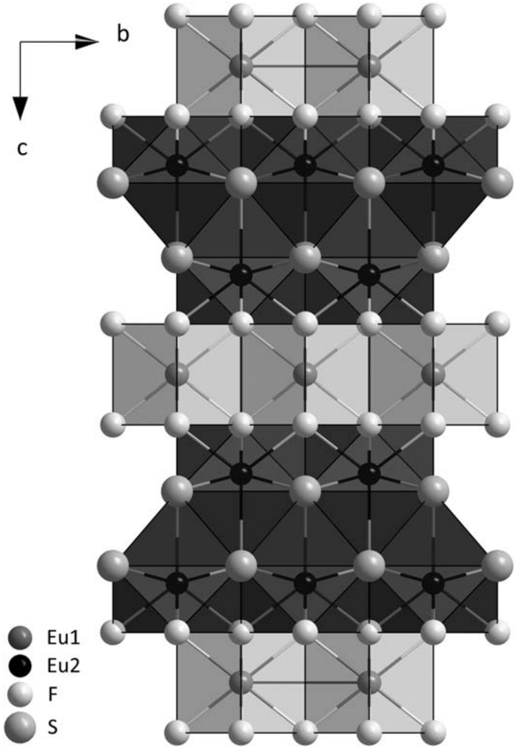

Fig. 1. View at the unit cell of $Eu_3F_4S_2$ as an ordered intergrowth model built up of EuF_2 slabs (light gray polyhedra) and EuFS slabs (dark gray polyhedra) extending parallel to the (001) plane in a 1:2 ratio according to $EuF_2 \cdot (EuFS)_2$.

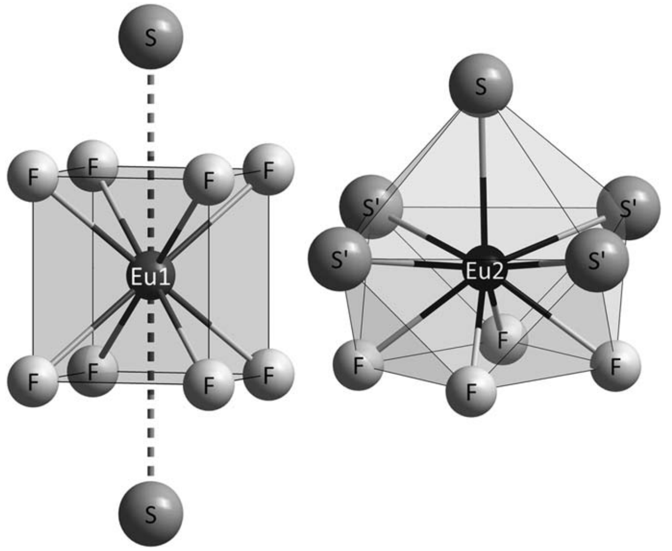

Fig. 2. Coordination polyhedra around the $(Eu1)^{2+}$ (left-hand side) and the $(Eu2)^{3+}$ cations (right-hand side) in the crystal structure of $Eu_3F_4S_2$.

four S^{2-} anions build a square antiprism. Its square plane of S^{2-} is capped by an additional S^{2-} anion at a slightly shorter distance (Fig. 2, right-hand part). This completes the coordination sphere leading to *CN*=9. Even the shape of the Eu1 and Eu2 coordination spheres match well with distinct Eu^{2+} and Eu^{3+} sites in $Eu_3F_4S_2$ ($\equiv [(Eu^{2+})(Eu^{3+})_2(F^-)_4(S^{2-})_2]$). Accordingly, Eu^{2+} should occupy the position of Eu1, because its coordination sphere $[(Eu1)F_8]$ coincides to the *fluorite*-type structure of EuF_2. Furthermore the eight distances $d(Eu1-F)$ of 255 pm match very well with those in EuF_2 (8 × 251 pm) [14,15] within experimental error. As a result Eu^{3+} is preferably expected on the site of Eu2, as its coordination polyhedron corresponds to that of A-EuFS [5]. This agrees with the course of the interatomic distances: 252 pm (4 × Eu2–F), 288 pm (4 × Eu2–S′), and 288 pm (1 × Eu2–S) in $Eu_3F_4S_2$ (Table 1); and 246 pm (4 × Eu–F), 277 pm (4 × Eu–S), and 282 pm (1 × Eu–S′) in A-EuFS [5].

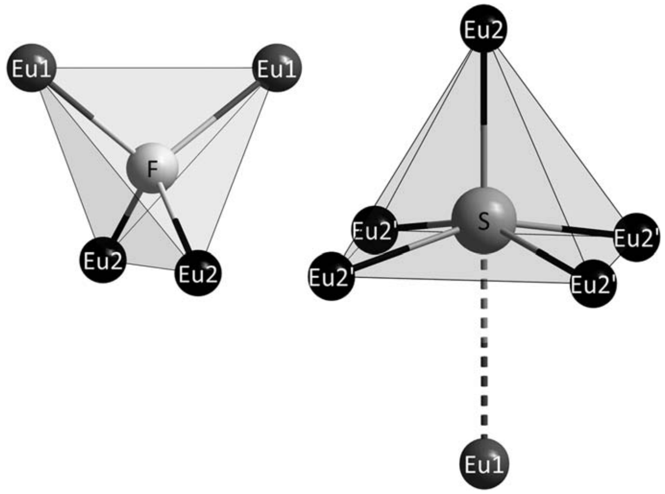

Fig. 3. Coordination environment around the F^- (left-hand side) and the S^{2-} anions (right-hand side) in the crystal structure of $Eu_3F_4S_2$.

Furthermore, the ordering of the Eu^{2+} cations at the positions within the square fluoride prism as well as the Eu^{3+} cations situated in the center of the monocapped square antiprism built of four fluoride and five sulfide anions can be confirmed, considering the respective valency using the bond–valence theory [21,22]. The contributions of the eight fluoride ligands (8 × 0.255) to the valency of Eu1 add up to a valency of 2.040 (the contribution of the two S^{2-} ligands at longer distances lies at 0.055 each, thus a contribution of 0.11 results, which does not change the calculated valency of Eu1 significantly), while for Eu2 four fluoride ligands with values of 0.220(4 ×) and five sulfide ligands of almost equal lengths showing values of 0.423(5 ×) summarize to a valency of 2.995. In the structure of A-EuFS the F^--centered $(Eu^{3+})_4$ tetrahedra are linked via four common edges forming $^2_\infty\{[(F^-)(Eu^{3+})_{4/4}]^{2+}\}$ layers. $Eu_3F_4S_2$ (Fig. 3, left-hand side) on the other hand has five common edges per $[FEu_4]$ tetrahedron (angles: $\sphericalangle$(Eu–F–Eu)=104°(2 ×) and 112°(4 ×)) within the double layers of the composition $^2_\infty\{([(F^-)(Eu1^{2+})_{2/8}(Eu2^{3+})_{2/4}]_4)^{4+}\}$. These correspond in an *anti*-isotypic manner to the double layers $^2_\infty\{([Cu(S1)_{2/8}(S2)_{2/4}]_4)^-\}$ of edge-sharing $[(Cu^{+/2+})(S^{2-})_4]$ tetrahedra in the crystal structure of KCu_4S_3 [23,24]. Finally, the sulfide anions are surrounded by five $(Eu2)^{3+}$ cations in the shape of a square pyramid with a (longer) sixth contact to one $(Eu1)^{2+}$ cation (Fig. 3, right-hand side), thus a coordination number of 5+1 results. These pyramids connect to adjacent pyramids via all eight edges. Starting from tetragonal EuFS (A-type with PbFCl structure) a step by step approach to the cubic CaF_2 structure of EuF_2 can be observed in tetragonal $Eu_3F_4S_2$, where the F^--centered $(Eu^{2+})_4$-tetrahedra are linked via all six edges to a three-dimensional network according to $^3_\infty\{[(F^-)(Eu^{2+})_{4/8}]\}$. However, the black color of $Eu_3F_4S_2$ indicates that the ordering of the different europium cations as described is only fictive. A localized mixed-valence should actually show just the color mixture of the components (A-EuFS: red; EuF_2: pale yellow).

A related structure is formed, however, by the isomorphic substitution of all Eu^{2+} cations by alkaline-earth metals according

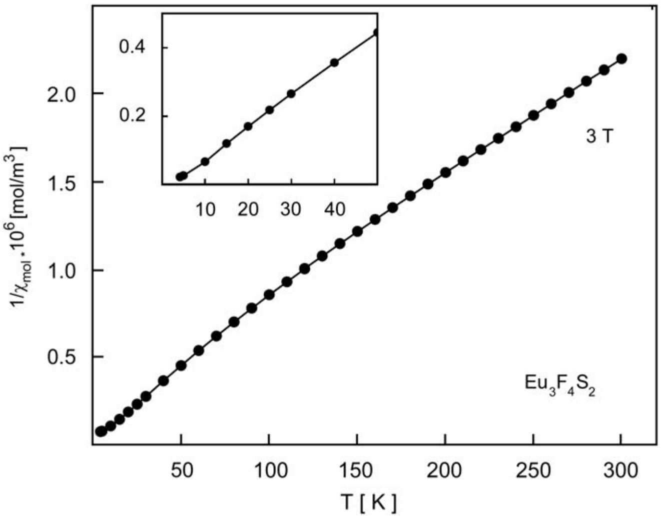

Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility of $Eu_3F_4S_2$ measured at an external field of 3 T. The low-temperature behavior is presented in the insert.

to $AEM_2F_4S_2$ (AE=Ca, Sr; M=Sm, Ce) [17,18], which are isotypic to the title compound. Nevertheless, even here a mixed occupation of the alkaline-earth metal(II) and the rare-earth metal(III) cations occurs according to *Demourges et al.* both on the 2*a* site in the center of the tetragonal fluoride prism and on the 4*e* site in the center of the monocapped square antiprism formed by fluoride and sulfide anions. This fact also underlines the aforementioned fiction of Eu^{2+}/Eu^{3+} ordering in $Eu_3F_4S_2$. The replacement of europium by other lanthanides that are not able to achieve a divalent oxidation state, the compensation of the additional positive charge has to be compensated by the substitution of one quarter of the fluoride by oxide anions as observed in $Er_3OF_3S_2$ [25]. In this structure, a symmetry reduction to the orthorhombic system takes place, since the replacement of Eu^{2+} by Er^{3+} goes along with a shrinking of the cationic size in the CaF_2-like part of the structure, which would force the surrounding F^- anions to arrange much closer than their doubled ionic radius. Consequently, this particular intergrowth-structure seems to be rather flexible, and thus can comply with the demands of different compositions such as both $(AE^{2+})(M^{3+})_2(F^-)_4(S^{2-})_2$ and $(M^{3+})_3(O^{2-})(F^-)_3(S^{2-})_2$.

3.2. *Magnetic Measurements*

The inverse magnetic susceptibility of $Eu_3F_4S_2$ is presented in Fig. 4 as a function of temperature. $Eu_3F_4S_2$ obeys the Curie–Weiss law above 20 K, however, a slight convex curvature is observed, indicating temperature independent contributions. Thus the data were fitted over the whole temperature range with a modified Curie–Weiss expression $\chi=\chi_0+C/(T-\Theta)$, resulting in an experimental magnetic moment of 8.19(5) μ_B/f.u., a paramagnetic Curie temperature (Weiss constant) of 0.3(2) K and a temperature-independent contribution χ_0 of 0.0092(3) cm^3/mol. The experimental magnetic moment per formula unit is close to the value of 7.94 μ_B for the free Eu^{2+} cation [26]. According to the ionic formula splitting $(Eu^{2+})(Eu^{3+})_2(F^-)_4(S^{2-})_2$, we expect one europium site with an electron configuration [Xe]4f^7 and another with [Xe]4f^6 in the ratio 1:2. This is consistent with the susceptibility data, where only one third of the europium atoms contribute to the paramagnetic behavior. No magnetic ordering could be detected down to 4.2 K.

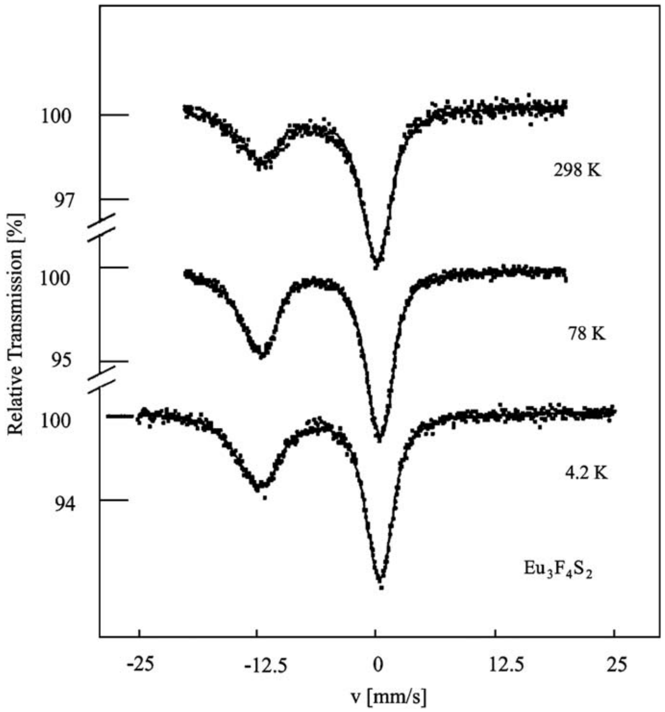

Fig. 5. Experimental and simulated ^{151}Eu-Mössbauer spectra of $Eu_3F_4S_2$ at 298, 78, and 4.2 K.

Table 3
^{151}Eu-Mössbauer fitting parameters for $Eu_3F_4S_2$ as a function of temperature.

Site	T (K)	δ (mm/s)	Γ (mm/s)	ΔE_Q (mm/s)	η	Fraction
Eu^{III}	298	0.12(6)	2.8(4)	6.5(18)	0.6(2)	0.64
Eu^{II}	298	−12.0(2)	4.8(5)	11.1(7)	0	0.36
Eu^{III}	78	0.44(3)	2.11(14)	6.2(5)	0.6(2)	0.63
Eu^{II}	78	−12.30(8)	2.8(3)	11.1(7)	0	0.37
Eu^{III}	4.2	0.42(4)	2.3(2)	5.7(13)	0.5(5)	0.62
Eu^{II}	4.2	−12.4(1)	3.8(6)	11.1(28)	0	0.38

The numbers in parentheses give the statistical errors in the last digit. Eu^{II}, signal for divalent europium; Eu^{III}, signal for trivalent europium; δ, isomer shift with respect to EuF_3; Γ, experimental line width; ΔE_Q, electric quadrupole interaction; η, asymmetry parameter.

3.2. *^{151}Eu-Mössbauer Spectroscopy*

The ^{151}Eu-Mössbauer spectra at 298, 78, and 4.2 K are presented in Fig. 5 together with transmission integral fits. All spectra could be well reproduced by a superposition of two signals with the fitted data listed in Table 3. The signals around −12 and 0.4 mm/s correspond to Eu^{2+} and Eu^{3+}, respectively. The ratio of these signals is roughly 1:2, in good accordance with the magnetic data and the above proposed ionic formula splitting. Again, the low-temperature measurements give no indication for magnetic ordering. Over the temperature range investigated, there is no hint for valence changes. Similar static mixed Eu^{II}/Eu^{III} valence has recently been observed for Eu_2CuS_3 [27], Eu_2SiN_3 [28], $Eu_5Sn_3S_{12}$ [29], or $Eu_5Zr_3S_{12}$ [30].

4. Conclusions

In this paper the synthesis and crystal structure of mixed-valent $Eu_3F_4S_2$ is described. The crystal structure can be interpreted as an intergrowth of CaF_2-type EuF_2 and PbFCl-type EuFS slabs according to $EuF_2 \cdot (EuFS)_2$. The positions of the Eu^{2+} and Eu^{3+} ions are ordered and can be determined by their anionic surrounding in the crystal structure. The static ordering of these sites was confirmed by ^{151}Eu-Mössbauer spectroscopy and magnetic susceptibility measurements. The magnetic and ^{151}Eu-Mössbauer spectroscopic data give no hint for magnetic no ordering down to 4.2 K. Thus, $Eu_3F_4S_2$ may be classified as a static mixed-valent system, regardless of its black color, which implies some polaron activities.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.08.023.

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