Structure, Magnetic Properties and $^{151}$Eu, $^{119}$Sn Mössbauer Spectroscopy of Eu$_5$Sn$_3$S$_{12}$ and Eu$_4$LuSn$_3$S$_{12}$

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Eu$_5$Sn$_3$S$_{12}$ and Eu$_4$LuSn$_3$S$_{12}$ were synthesized and their structures refined from single crystal data ($Pmc2_1$, Eu$_5$Sn$_3$S$_{12}$: $a = 3.908(1)$, $b = 20.115(4)$, $c = 11.451(2)$ Å; $wR2 = 0.0519$ for 3048 $F^2$ and 122 parameters; Eu$_4$LuSn$_3$S$_{12}$: $a = 3.920(1)$, $b = 20.132(4)$, $c = 11.459(2)$ Å; $wR2 = 0.0737$ for 3298 $F^2$ and 122 parameters). The structures contain one-dimensional chains of edge-sharing SnS$_2$S$_4$/2 octahedra and corner-sharing SnS$_3$S$_2$/2 trigonal bipyramids, running parallel to [100]. Five europium sites are seven- or eightfold coordinated by sulfur atoms. Lutetium atoms in Eu$_4$LuSn$_3$S$_{12}$ show a strong site preference for one of the two Eu$^{3+}$ positions of Eu$_5$Sn$_3$S$_{12}$ and no structural disorder was observed. Both compounds show static mixed valence according to Eu$^{2+}$3Eu$^{3+}$2Sn$^{4+}$3S$_{12}^-$ and Eu$^{2+}$3Lu$^{3+}$3Sn$^{4+}$2S$_{12}^-$, which was confirmed by temperature dependent magnetic susceptibility measurements. The experimental magnetic moments of 14.6(1) (Eu$_5$Sn$_3$S$_{12}$) and 14.1(1) (Eu$_4$LuSn$_3$S$_{12}$) $\mu_B$/f.u. indicate that each of the two sulfides contains three divalent europium atoms per formula unit. Magnetic ordering for Eu$_5$Sn$_3$S$_{12}$ and Eu$_4$LuSn$_3$S$_{12}$ sets in below 5 and 3 K, respectively. Both sulfides show metamagnetic or spin-flip transitions in the magnetization curves at 3 K (2 K) with full saturation of the europium magnetic moments at 3 K (2 K) and 80 kOe. $^{151}$Eu Mössbauer spectra fully confirm the Eu$^{2+}$ and Eu$^{3+}$ site occupancies. At 4.2 K an increase in line width indicates small hyperfine fields at the europium nuclei.

Key words: Europium Compounds, Mixed Valence, Magnetism, Mössbauer Spectroscopy