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PHYSICAL METHODS OF INVESTIGATION

Crystal Structures of $EuLnCuS_3$ (Ln = Nd and Sm)[1]

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Abstract—The compound sulfides $EuLnCuS_3$ (Ln = Nd and Sm) were obtained for the first time. Their crystal structures were determined from X-ray powder diffraction data. The crystals of both compounds are orthorhombic (space group *Pnma*). The compound $EuNdCuS_3$ is isostructural with $BaLaCuS_3$; the unit cell parameters are $a = 11.0438(2)$ Å, $b = 4.0660(1)$ Å, $c = 11.4149(4)$ Å. The compound $EuSmCuS_3$ is isostructural with Eu_2CuS_3; the unit cell parameters are $a = 10.4202(2)$ Å, $b = 3.9701(1)$ Å, $c = 12.8022(2)$ Å.

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In [1], the compound sulfides $EuLnCuS_3$ (Ln = Gd–Lu) have been obtained by solid-state reactions of rare-earth metal(III) oxides (Ln_2O_3) with cupric oxide (CuO). Stoichiometric mixtures of the starting reagents were heated in a graphite boat at 1170–1320 K in a flow of a mixture of gaseous CS_2 and N_2 prepared by bubbling N_2 through liquid CS_2 at room temperature. The synthesis included several steps of grinding the resulting product. This method proved to be unsuitable for the synthesis of the phase $EuNdCuS_3$; in addition, samples with Ln = Sm, Ho, and Er contained $(Eu, Ln)_2O_2S$ as impurities (> 3%). The crystallochemical characteristics of the compound sulfides $EuLnCuS_3$ (Ln = Gd–Lu) were determined from the X-ray powder diffraction data. It was demonstrated that the transformation of $EuLnCuS_3$ from the structural type Eu_2CuS_3 (space group *Pnma*; Ln = Gd–Dy) into the structural type $KZrCuS_3$ (space group *Cmcm*; Ln = Tm–Lu) depends on the size of the rare-earth metal ion. The magnetic properties of the above sulfides were studied. For the compounds $EuLnCuS_3$ (Ln = Y, Eu, and Lu) containing nonmagnetic Ln ions, ferromagnetic ordering of the Eu^{2+} moments occurs at 3.4–4.4 K. The compounds $EuLnCuS_3$ containing magnetic Ln ions undergo a ferrimagnetic transition at ca. 5.0 K [1].

No crystallographic data for $EuLnCuS_3$ (Ln = Nd and Sm) are available from the literature. The presence of *d*- and *f* elements in a crystal lattice can impart a number of practically useful properties to these compound sulfides. The goal of this study was to obtain the compounds $EuLnCuS_3$ (Ln = Nd and Sm) and determine their crystal structures from X-ray powder diffraction data.

EXPERIMENTAL

Cuprous sulfide was prepared from elemental Cu (special purity grade 11-4) and elemental S (special purity grade 15-3) in sealed evacuated double-walled quartz tubes. The sulfides EuS, Nd_2S_3, and Sm_2S_3 were prepared from appropriate oxides (EvO-Zh, NO-D, and SmO-G grades, respectively) in a flow of H_2S and CS_2 at 1300 K [2]. According to X-ray powder diffraction data, the simple sulfides are single-phase compounds. They have stoichiometric formulas to within the chemical analysis error. The compound sulfides $EuLnCuS_3$ (Ln = Nd and Sm) were obtained by fusing mixtures of the starting sulfides ($EuS : Ln_2S_3 : Cu_2S = 2 : 1 : 1$) in graphite crucibles placed in sealed evacuated double-walled quartz tubes. The tubes were heated in an electric furnace to 1570 K and kept for 30 min. Then the furnace was turned off for cooling. Samples were annealed in sealed evacuated quartz tubes at 970 K for 3000 h.

To check the sample homogeneity, we determined the element distribution at five different surface areas of $EuLnCuS_3$ samples (Ln = Nd and Sm) using a Philips SEM 515 microscope (provided by the Tomsk Collective Use Center of Materials Science (TCUCMS)). The composition of all the areas under analysis corresponded to the formula $EuLnCuS_3$. The element distribution map over the sample for the analyzed areas shows no accumulation of any element (i.e., each element is uniformly distributed throughout the sample surface). Using a Quanta 200 3D system (provided by TCUCMS) with electron and focused ion beams, we made a cross section and analyzed the chemical composition. The composition of the undersurface layers have the formula $EuLnCuS_3$.

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[1] The results of this study have been presented at the X International Scientific Conference “Solid-State Chemistry: Nanomaterials, Nanotechnologies” (Stavropol, October 17–22, 2010) [11] and the All-Russia Scientific Conference “Challenges of Modern Chemistry. Theory and Practice” (Ufa, October 21–23, 2010) [12].

Table 1. Crystallographic parameters of $EuNdCuS_3$ and $EuSnCuS_3$

Formula	$EuNdCuS_3$	$EuSmCuS_3$
Space group	*Pnma*	*Pnma*
a, Å	11.0438(2)	10.4202(2)
b, Å	4.0660(1)	3.9701(1)
c, Å	11.4149(4)	12.8022(2)
V, Å^3	512.58(2)	529.62(2)
Z	4	4
ρ_{calc}, g/cm^3	5.908	5.795
Structural type	$BaLaCuS_3$	Eu_2CuS_3
T, K	298	298
λ, Å	1.789010	1.789010
2θ, deg	10–125	10–125
h, k, l	$0 \le h \le 10,\ 0 \le k \le 4,\ 0 \le l \le 11$	$0 \le h \le 10,\ 0 \le k \le 3,\ 0 \le l \le 12$
R-DDM, %	8.49	8.73
R_{Bragg}, %	4.6	4.7

The individuality of the compounds obtained was confirmed by electron-probe microanalysis and X-ray powder diffraction. Electron-probe microanalysis was carried out on a METAM PB microscope. X-ray powder diffraction was examined on a PANalytical X'Pert PRO diffractometer fitted with a PIXcel detector (CoK_α radiation). According to X-ray powder diffraction data, the content of the foreign phases in the samples do not exceed 4 wt %. The lattice parameters of $EuLnCuS_3$ (Ln = Nd and Sm) were determined with the ITO program [3]. The powder diffraction data were used to refine the crystal structures by the derivative difference minimization (DDM) method [4] with allowance for the effects of predominant orientation, anisotropic peak broadening, and sample surface roughness. Data for the isostructural compounds $BaLaCuS_3$ [5, 6] and Eu_2CuS_3 [7, 8] were employed as initial models. Crystallographic parameters and the data collection and refinement statistics are given in Table 1. Experimental, calculated, and difference X-ray diffraction patterns are shown in Fig. 1. Atomic coordinates and isotropic thermal parameters are listed in Tables 2 and 3. The crystallographic data were used to calculate the main shortest anion–cation distances (Tables 4, 5). The crystal structures were visualized with the Diamond 3 software [9].

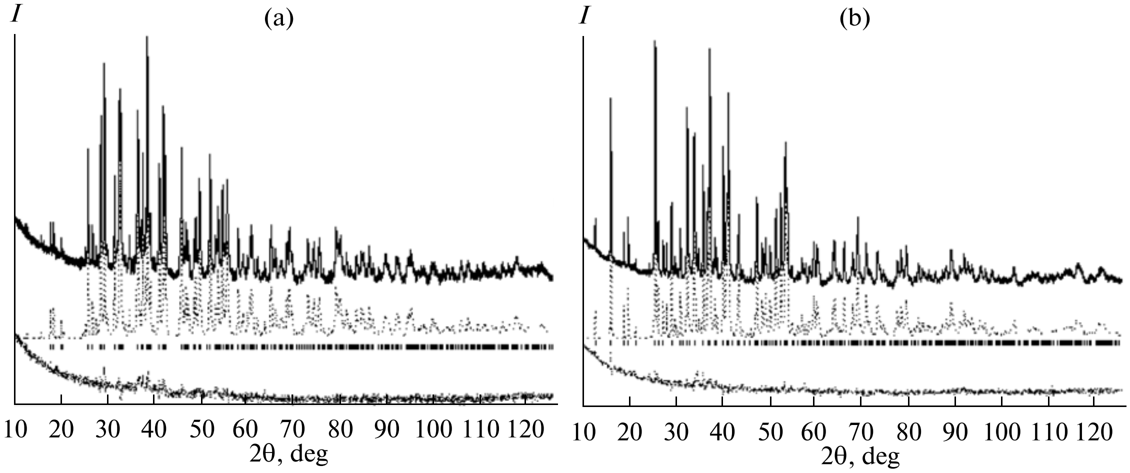

Fig. 1. Experimental (solid line), calculated (dashed line), and difference X-ray diffraction patterns (dotted lines) of (a) $EuNdCuS_3$ and (b) $EuSmCuS_3$ for the DDM-refined structures. The positions of the peaks of the main phase are indicated with primes.

Table 2. Atomic coordinates and thermal parameters in the structure of EuNdCuS$_3$

Atom	x	y	z	U, Å^2
Eu	0.6834(2)	1/4	0.0043(2)	0.013(1)
Nd	0.0107(2)	1/4	0.8172(2)	0.013(1)
Cu	0.2557(4)	1/4	0.2129(4)	0.020(2)
S(1)	0.1151(8)	1/4	0.0579(8)	0.013(3)
S(2)	0.4512(7)	1/4	0.1396(8)	0.015(3)
S(3)	0.2765(7)	1/4	0.8084(8)	0.015(3)

Table 3. Atomic coordinates and thermal parameters in the structure of EuSmCuS$_3$

Atom	x	y	z	U, Å^2
Eu	0.7840(2)	1/4	0.0019(2)	0.0143(8)
Sm	0.0166(2)	1/4	0.7355(1)	0.0108(6)
Cu	0.2334(3)	1/4	0.2225(3)	0.017(1)
S(1)	0.0482(6)	1/4	0.1176(5)	0.011(2)
S(2)	0.4040(7)	1/4	0.1021(4)	0.015(2)
S(3)	0.2591(6)	1/4	0.8263(5)	0.011(2)

RESULTS AND DISCUSSION

The crystal structures of the compounds obtained are shown in Fig. 2. They have layered block structures. Each copper ion is coordinated to four S atoms making up a distorted tetrahedron. The vertices of the CuS$_4$ tetrahedra are occupied by the S(1), S(2), and two S(3) atoms, the average Cu–S bond lengths being 2.335 (EuNdCuS$_3$) and 2.371 Å (EuSmCuS$_3$). These bond lengths are somewhat shorter than a theoretical value of 2.44 Å because of the presence of covalent bonding. In both structures, the CuS$_4$ tetrahedra are joined in pairs to produce continuous chains along the direction [010] (axis b), sharing the S(3) vertices. The Ln atoms coordinated by the S atoms are between the chains of the CuS$_4$ tetrahedra. The Eu and Ln ions occupy two crystallographically independent positions.

In both structures, the Eu ions coordinate seven sulfur ions between the layers of CuLnS$_3$ to form the monocapped trigonal prism EuS$_7$ (CN = 6 + 1). The prisms share two faces along the axis b and edges along the axis a to form 2D networks in the plane ba. The prism EuS$_7$ consists of the atoms 2S(1) + 2S(2) + S(2) + 2S(3) in EuSmCuS$_3$ and the atoms S(1) + 2S(1) + 2S(2) + 2S(3) in EuSmCuS$_3$. The average Eu–S bond lengths are 3.024 and 3.059 Å, respectively; the theoretical bond length is 3.04 Å [10]. With a decrease in the Ln^{3+} ion radius, the Eu–S bonds on average become lengthened (Tables 4, 5; Fig. 3). This suggests that the local environment of the Eu atom tends to transform its geometry and change the structural type, which is confirmed by the previous data for EuLnCuS$_3$ (Ln = Gd–Lu) [1].

In EuNdCuS$_3$, the coordination polyhedron of the Nd atom is a monocapped trigonal prism (CN = 6 + 1) (Fig. 3) made up of the atoms S(1) + 2S(1) + 2S(2) + S(3) + S(3), the average Nd–S bond length being 2.910 Å. The theoretical bond lengths are 2.823 (for CN = 6) and 2.949 Å (for CN = 8) [10]. The prisms NdS$_7$ form a 3D structure with channels housing Eu and Cu ions. The prisms are joined in pairs along the axis c, sharing the edges 2S(1)S(1) to form continuous chains along the direction [010]. The prisms share the edges 2S(1)S(2) with similar prisms NdS$_7$ and are linked by the vertices 2S(3) along the axis a.

In EuSmCuS$_3$, the Sm atoms located between the chains of CuS$_4$ tetrahedra have an octahedral environment: 2S(1) + 2S(2) + S(3) + S(3) (Fig. 3). The average Sm–S bond length is 2.798 Å, which is somewhat shorter than the theoretical value (2.798 Å [10]). The distorted octahedra SmS$_6$ share the edges 2S(2)S(1) along the axis b and the vertices 2S(3) along the axis a to form 2D networks in the ba plane. The octahedra SmS$_6$ and the tetrahedra CuS$_4$ produce a layer of CuSmS$_3$ perpendicular to axis c (as viewed along the axis b). In the layer of CuSmS$_3$, the octahedra SmS$_6$

Table 4. Bond lengths d in the structure of EuNdCuS$_3$

Bond	d, Å	Bond	d, Å	Bond	d, Å
Eu–S(1)	2 × 3.096(7)	Nd–S(1)	1 × 2.979(9)	Cu–S(1)	1 × 2.354(9)
Eu–S(2)	2 × 3.007(7)	Nd–S(1)	2 × 2.845(7)	Cu–S(2)	1 × 2.316(9)
Eu–S(2)	1 × 2.994(8)	Nd–S(2)	2 × 2.902(9)	Cu–S(3)	2 × 2.334(5)
Eu–S(3)	2 × 2.983(7)	Nd–S(3)	1 × 2.938(8)	***⟨Cu–S⟩***	***2.335***
⟨Eu–S⟩	***3.024***	Nd–S(3)	1 × 2.957(8)		
		⟨Nd–S⟩	***2.910***		

Table 5. Bond lengths d in the structure of $EuSmCuS_3$

Bond	d, Å	Bond	d, Å	Bond	d, Å
Eu–S(1)	1 × 3.127(7)	Sm–S(1)	2 × 2.817(5)	Cu–S(1)	1 × 2.351(7)
Eu–S(1)	2 × 3.056(5)	Sm–S(2)	2 × 2.746(4)	Cu–S(2)	1 × 2.354(8)
Eu–S(2)	2 × 3.090(6)	Sm–S(3)	1 × 2.782(7)	Cu–S(3)	2 × 2.390(4)
Eu–S(3)	2 × 2.996(5)	Sm–S(3)	1 × 2.797(7)	***⟨Cu–S⟩***	***2.371***
⟨Eu–S⟩	***3.059***	***⟨Sm–S⟩***	***2.784***		

share the vertices with each other and share the edges with the tetrahedra CuS_4.

With a decrease in the Ln^{3+} ion radius, the Ln–S bonds (Nd–S, 2.910 Å; Sm–S, 2.784 Å) become shorter, while the average Cu–S bond length slightly increases. This is accompanied by a decrease in the unit cell parameters a and b and an increase in the parameter c (Table 1). Similar trends have been observed for the unit cell parameters of other isomorphic compounds: $EuLnCuS_3$ (Ln = Eu, Gd–Lu) [1, 7, 8] and $BaLnMQ_3$ (M = Cu, Ag, and Au; Q = S, Se, and Te) [5, 6].

To sum up, the structure of $EuSmCuS_3$ consists of 2D layers ($CuSmS_3$) in the ba plane, which are made

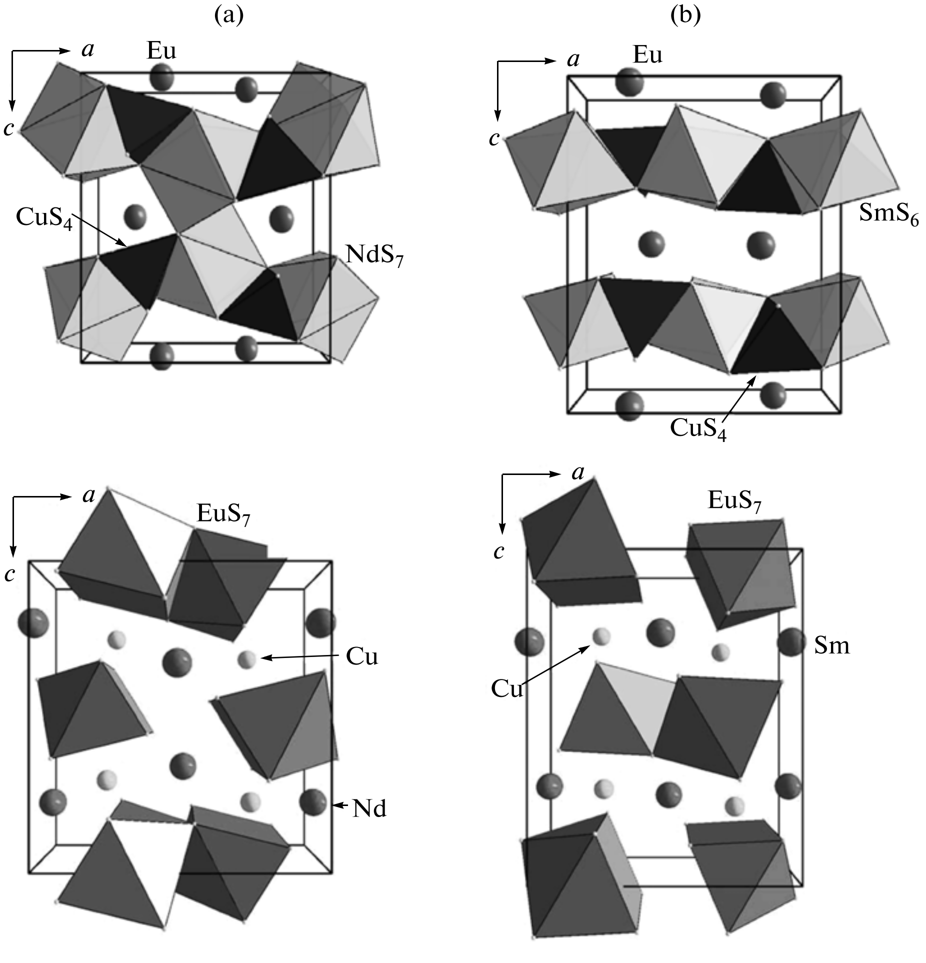

Fig. 2. Projections of the structures of (a) $EuNdCuS_3$ and (b) $EuSmCuS_3$ along the [010] direction.

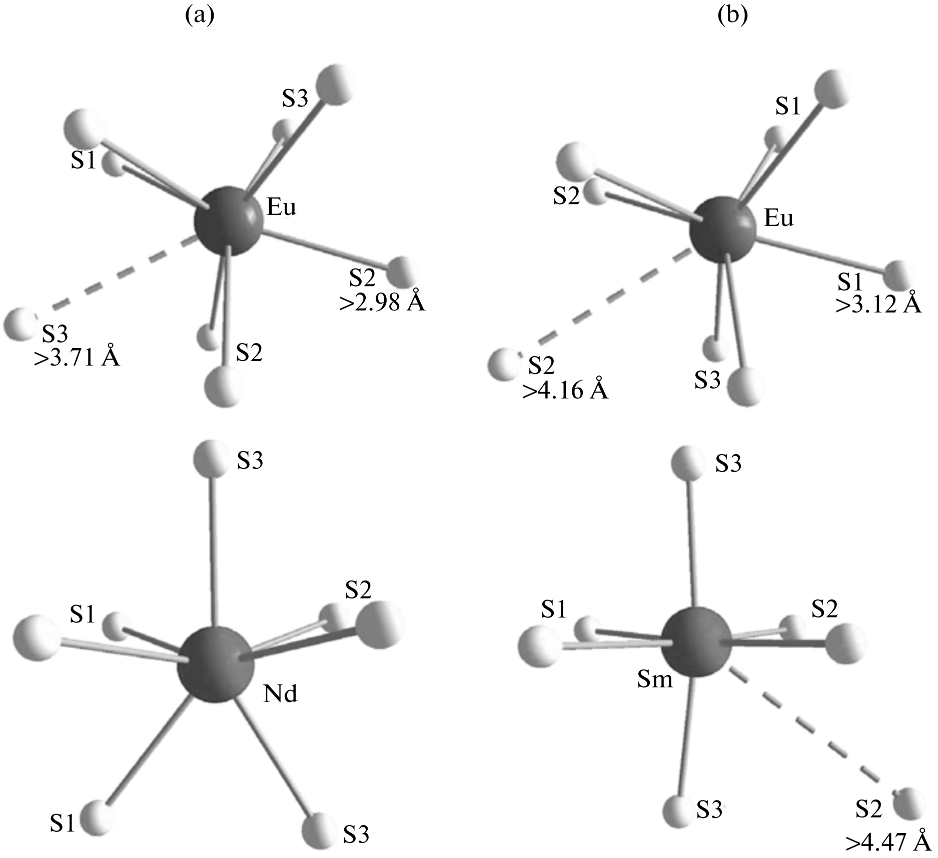

Fig. 3. Coordination of Eu and Ln in (a) $EuNdCuS_3$ and (b) $EuSmCuS_3$.

up of distorted CuS_4 tetrahedra and SmS_6 octahedra with Eu ions between them. The structure of $EuNdCuS_3$ is a 3D framework ($CuNdS_3$) constructed from distorted CuS_4 tetrahedra and monocapped trigonal prisms NdS_7 with Eu ions between them. The crystals of the compounds studied have the identical symmetry and the same set of atomic positions but they differ in the bonding system and the coordination of Nd and Sm.

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