

## PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

# Cu<sub>2</sub>S–EuS Phase Diagram<sup>1</sup>

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**Abstract**—In the Cu<sub>2</sub>S–EuS system, a eutectic is formed between Cu<sub>2</sub>S- and EuS-based solid solutions (ss) at (1069 ± 2) K, 24.5 mol % EuS. EuS dissolves 7.0 (at 1770 K), 5.0 (1170 K), and 3.0 (770 K) mol % Cu<sub>2</sub>S. A β-Cu<sub>2</sub>S-based ss is of the open type, has an extent (mol %) of 15.5 (at 1069 K), 7.5 (970 K), 4.5 (770 K), 2.5 (520 K), and 1.5 (379 K) EuS, and melts incongruently at 1186 K, 7.0 mol % EuS. α-Cu<sub>2</sub>S at 379 K dissolves 6.5 mol % EuS; γ-Cu<sub>2</sub>S at (1186 ± 3) K dissolves 3.5 mol % EuS.

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Sulfide EuS is formed upon treatment of EuO in a flow of H<sub>2</sub>S and CS<sub>2</sub> [1], has a NaCl-type cubic lattice (space group *Fm3m*) with the unit cell parameter  $a = 0.5970$  nm [2], and melts congruently at 2250 [2] or 1900°C [3]. Cu<sub>2</sub>S is prepared from the constituent elements by an ampoule technique; it melts congruently at 1402 K and exists in three polymorphs [4]. The low-temperature α-Cu<sub>2</sub>S phase having an orthorhombic unit cell with  $a = 1.350$  nm,  $b = 2.732$  nm,  $c = 1.185$  nm [5] transforms at 376 K to a medium-temperature β-Cu<sub>2</sub>S phase, which is hexagonal with  $a = 0.396$  nm,  $c = 0.678$  nm [6]. The transition from β-Cu<sub>2</sub>S to FCC γ-Cu<sub>2</sub>S occurs at ~708 K. High-temperature phases are not quenchable [4]. No data on the Cu<sub>2</sub>S–EuS phase diagram has been found in the literature.

The existence of a hypothetical system in which a field of an open-type β-Cu<sub>2</sub>S-based solid solution (ss) is formed was predicted on the basis of analysis of phase equilibria in Cu<sub>2</sub>S–Ln<sub>2</sub>S<sub>3</sub> systems [4, 7]. No experimental proof of this hypothesis has been obtained.

Here, we study phase equilibria in the Cu<sub>2</sub>S–EuS system along polytherms at 350, 520, 770, 970, 1170, and 1770 K to construct a phase diagram of this system.

### EXPERIMENTAL

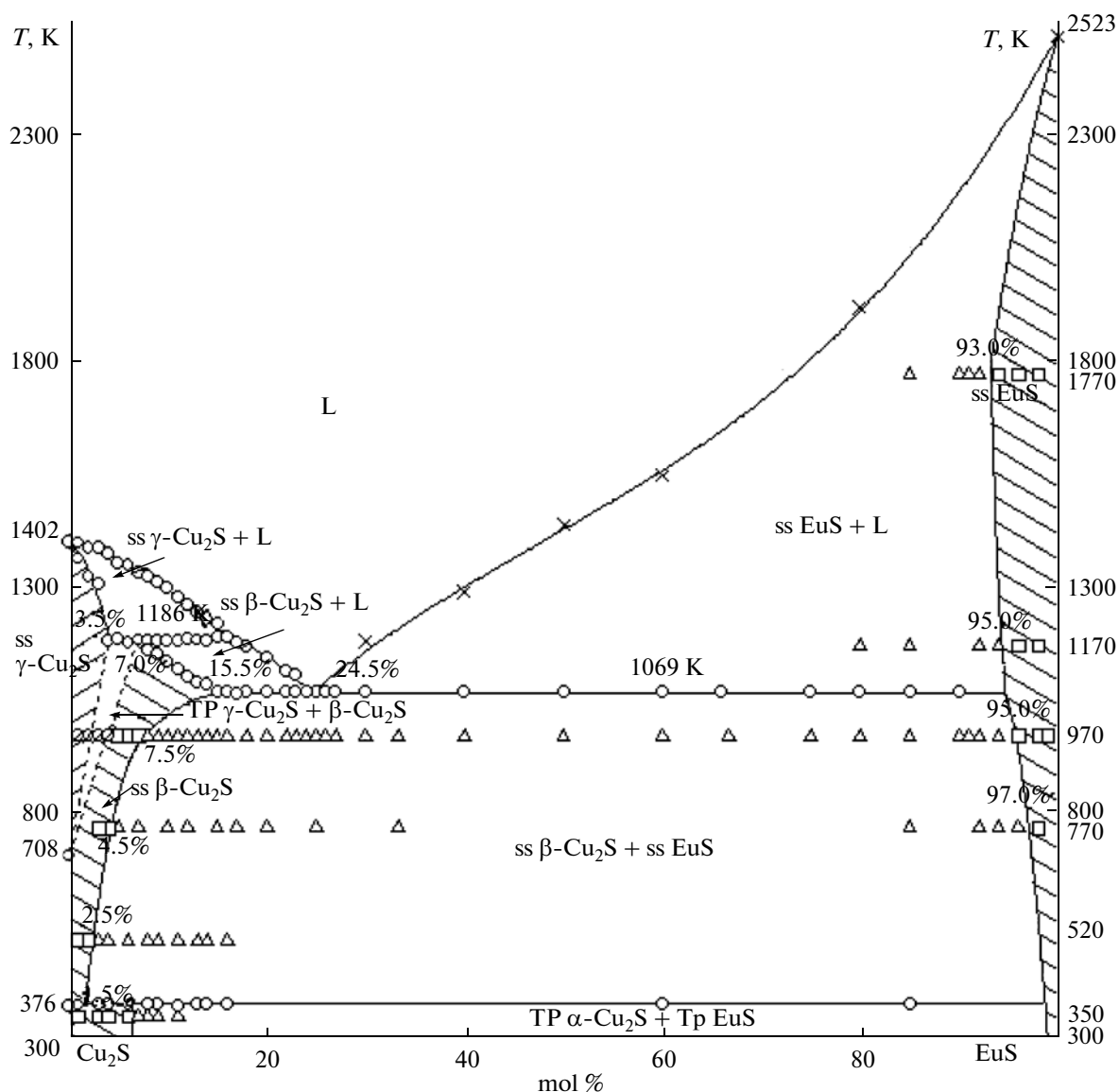
Cu<sub>2</sub>S was prepared from the constituent elements (copper of 11–4 high purity grade and sulfur of 15–3 high purity grade) in double evacuated and sealed-off silica ampoules. EuS was prepared from europium oxide of EvO–Zh type in an H<sub>2</sub>S and CS<sub>2</sub> flow at 1300 K for 5 h [1].

Forty one Cu<sub>2</sub>S–EuS samples of diverse chemical compositions were prepared from the constituent sul-

fides. Cast samples containing 1.0–60.0 mol % EuS were prepared by alloying the batch inside graphite crucibles placed in evacuated and sealed-off silica ampoules. The ampoules were heated to a temperature ranging from 1170 to 1580 K (depending on the sample), exposed for 30 min, and then furnace-cooled. Slightly melted and sintered samples having compositions of 66.6(6)–99.0 mol % EuS were prepared in an uncovered reactor using induction heating of a graphite crucible placed in a high-frequency generator. These samples were annealed at 970 K for 1440 h. In order to determine homogeneity regions based on Cu<sub>2</sub>S and EuS polymorphs, samples were annealed inside an electrically heated furnace in evacuated silica ampoules at 350 K for 3 years, at 520 K for 2 years, at 770 K for 6 months, and at 1170 K for 1 month. At 1770 K samples were annealed for 0.5 h. Annealing temperatures in muffle furnaces were adjusted with an accuracy of ±5 K using a Thermolux thermal controller. Equilibration was judged from the results of microstructure observations (MSA), X-ray powder diffraction (XRD), and differential scanning calorimetry (DSC) carried out in the course of annealing. Eighty nine samples altogether were studied by physicochemical methods taking into account annealing.

A thermoanalytical experiment was carried out on a Setsys Evolution 1750 (TGA-DSC 1600) setup according to a previously worked out procedure using the SETSOFT 2000 program package [8] and a Pt/Pt–Rh (10%) thermocouple, which operates in the temperature range 220–1870 K. Overlapping peaks were resolved using the Thermogram Analyser software. Visual polythermal analysis (VPTA) was carried out with an error 1% of the measured value. Microstructure examination (MSA) was carried out with a METAM PB-22 microscope. Durometric analysis was performed on a PMT-3 hardness meter using the Wickers method with an error of 5–7%. The Edstate 2D program was used in graphical constructions. X-ray powder diffraction (XRD) was measured on a

<sup>1</sup> The results of this study were communicated at the 17th International Conference on Chemical Thermodynamics (Kazan, June 29 through July 3, 2009) [11].



**Fig. 1.** Cu<sub>2</sub>S–EuS phase diagram: (○) DSC data, (⊙) compositions of samples for which there were no methods for determining their phase compositions under annealing conditions, and (×) VPTA data. The state of a sample according to X-ray powder diffraction and MSA: (□) a single phase and (△) two phases.

DRON-7 diffractometer (CuK<sub>α</sub> radiation;  $\lambda = 1.54184 \text{ \AA}$ ; Ni filter) in the range  $10^\circ \leq 2\theta \leq 100^\circ$ .

## RESULTS AND DISCUSSION

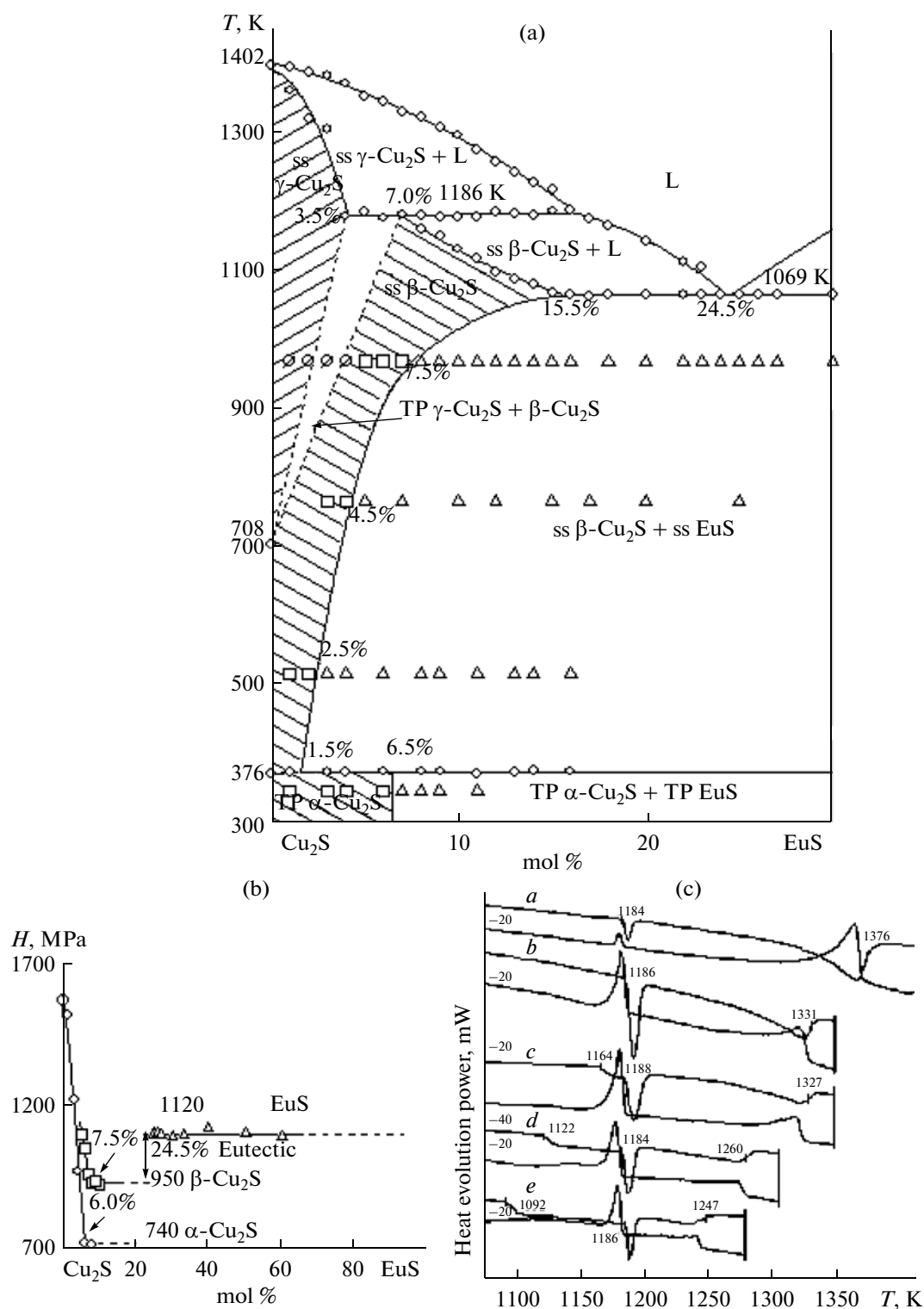
The Cu<sub>2</sub>S–EuS phase diagram is of the eutectic type with open fields of  $\beta$ -Cu<sub>2</sub>S-based and  $\alpha$ -Cu<sub>2</sub>S ss and a closed field of  $\gamma$ -Cu<sub>2</sub>S-based ss (Figs. 1, 2).

The  $\alpha$ -Cu<sub>2</sub>S-based ss is of the open type; its boundary compositions are in equilibrium with EuS ss. As shown by MSA, samples containing 1.0, 3.0, 4.0, or 6.0 mol % EuS that were annealed at 350 K are homogeneous. Their microstructures are represented by individual blocks, which are separated by well-defined cracks. When exposed to HCl (1 : 10), the surface

within individual blocks is etched uniformly. The degree of etching varies from block to block.

The samples containing 7.0, 8.0, 9.0, or 11.0 mol % EuS are comprised of two phases (Fig. 3). In the bulk and along  $\alpha$ -Cu<sub>2</sub>S grain boundaries, there are fine acicular inclusions of gray-colored EuS grains having sizes of 5–70  $\mu\text{m}$ , which are etchable by HCl. EuS grains are formed as filamentary branches. The ss boundary according to MSA is 6.5 mol % EuS.

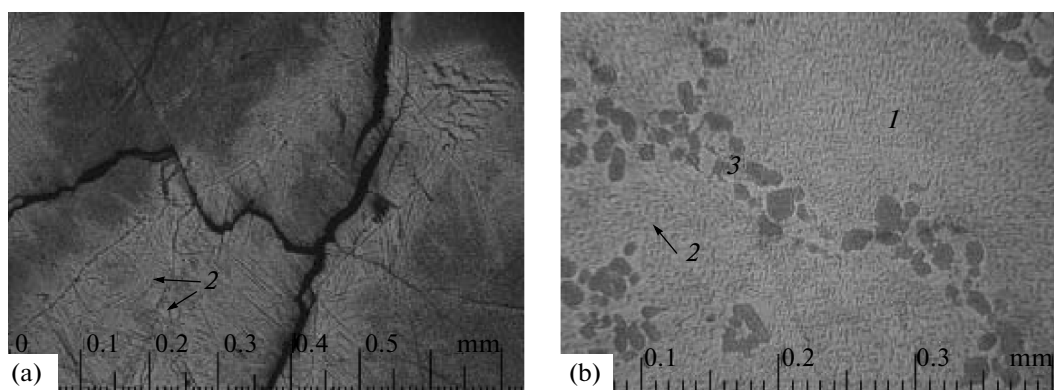
In the  $\alpha$ -Cu<sub>2</sub>S-based ss, weak reflections are systematically reduced in intensity; at the same time, the reflections ( $d_{hkl}$ : 1 11 1; 345) noticeably grow in intensity, and in addition a reflection with an interplanar spacing of 3.08  $\text{\AA}$  appears. The positions of the grow-



**Fig. 2.** Panel (a): a fragment of the Cu<sub>2</sub>S–EuS phase diagram (for the legend, see Fig. 1). Panel (b): microhardness versus composition curve for Cu<sub>2</sub>S–EuS samples (*P* = 0.02 kg): (○) α-Cu<sub>2</sub>S ss quenched from 350 K; (□) β-Cu<sub>2</sub>S ss quenched from 970 K; and (△) EuS ss. Panel (c): differential thermal curves for Cu<sub>2</sub>S–EuS samples containing: (a) 4.0, (b) 7.0, (c) 8.0, (d) 11.0, and (e) 13.0 mol % EuS. All samples were annealed at 970 K.

ing reflections corresponds to the strongest reflections from a Cu<sub>2</sub>Ln<sub>2/3</sub>S<sub>2</sub>-type structure in Cu<sub>2</sub>S–Ln<sub>2</sub>S<sub>3</sub> (Ln = Dy, Er) systems [7, 9]. The evolution of X-ray

diffraction intensities implies the appearance in the α-Cu<sub>2</sub>S-based ss of structural motifs characteristic of the Cu<sub>2</sub>Ln<sub>2/3</sub>S<sub>2</sub> phase (Fig. 4).



**Fig. 3.** Microphotographs of Cu<sub>2</sub>S–EuS samples: (a) 8 mol % EuS, annealing at 350 K, etching with HCl; and (b) 18.0 mol % EuS, annealing at 970 K. Phases and phase combinations occurring in the system: (1) the solid solution based on a Cu<sub>2</sub>S polymorph; (2) EuS ss crystals formed as a result of the exsolution of the primary Cu<sub>2</sub>S-based ss; and (3) the eutectic formed by crystals of EuS-based and Cu<sub>2</sub>S-based ss phases.

During thermal analysis, weighed portions of samples containing 1.0–11.0 mol % EuS were subjected to isothermal exposure for 1 h 30 min at 350 K to remove possible trace water. All thermoanalytical curves feature increased onset temperatures of peaks, which indicates the existence of a peritectoid phase transformation in the system (Fig. 2). The peritectoid temperature averaged over eight samples is 379 K (table).

The  $\beta$ -Cu<sub>2</sub>S-based ss is of the open type and is in equilibrium with EuS ss over the entire range of temperatures from the peritectoid temperature (379 K) to the eutectic temperature (1069 K). The solvus coordinates were determined by studying samples that were annealed at 520, 770, or 970 K.

The ratio between the time for which the samples were annealed at 520 K (2 years) and the time taken to cool them to room temperature (less than 1 min) and the results of physicochemical studies of the samples, imply that the phase-grain composition of the samples does not change upon cooling. However, the Cu<sub>2</sub>S phases change their structures during cooling. In the samples containing 1.0 or 2.0 mol % EuS, the  $\alpha$ -Cu<sub>2</sub>S structure was identified. Reflections from the structural motif of the Cu<sub>2</sub>Ln<sub>2/3</sub>S<sub>2</sub> phase virtually do not appear in the X-ray diffraction patterns of these samples; they appear in the  $\alpha$ -Cu<sub>2</sub>S-based ss. According to MSA, the samples containing 1.0 or 2.0 mol % EuS are single

phases, whereas the sample containing 3 mol % EuS distinctly comprises two phases. In the samples with 4.0–8.0 mol % EuS, the amount and size of acicular EuS grains increase systematically (to reach 200  $\mu$ m). The ss boundary is set to lay at 2.5 mol % EuS.

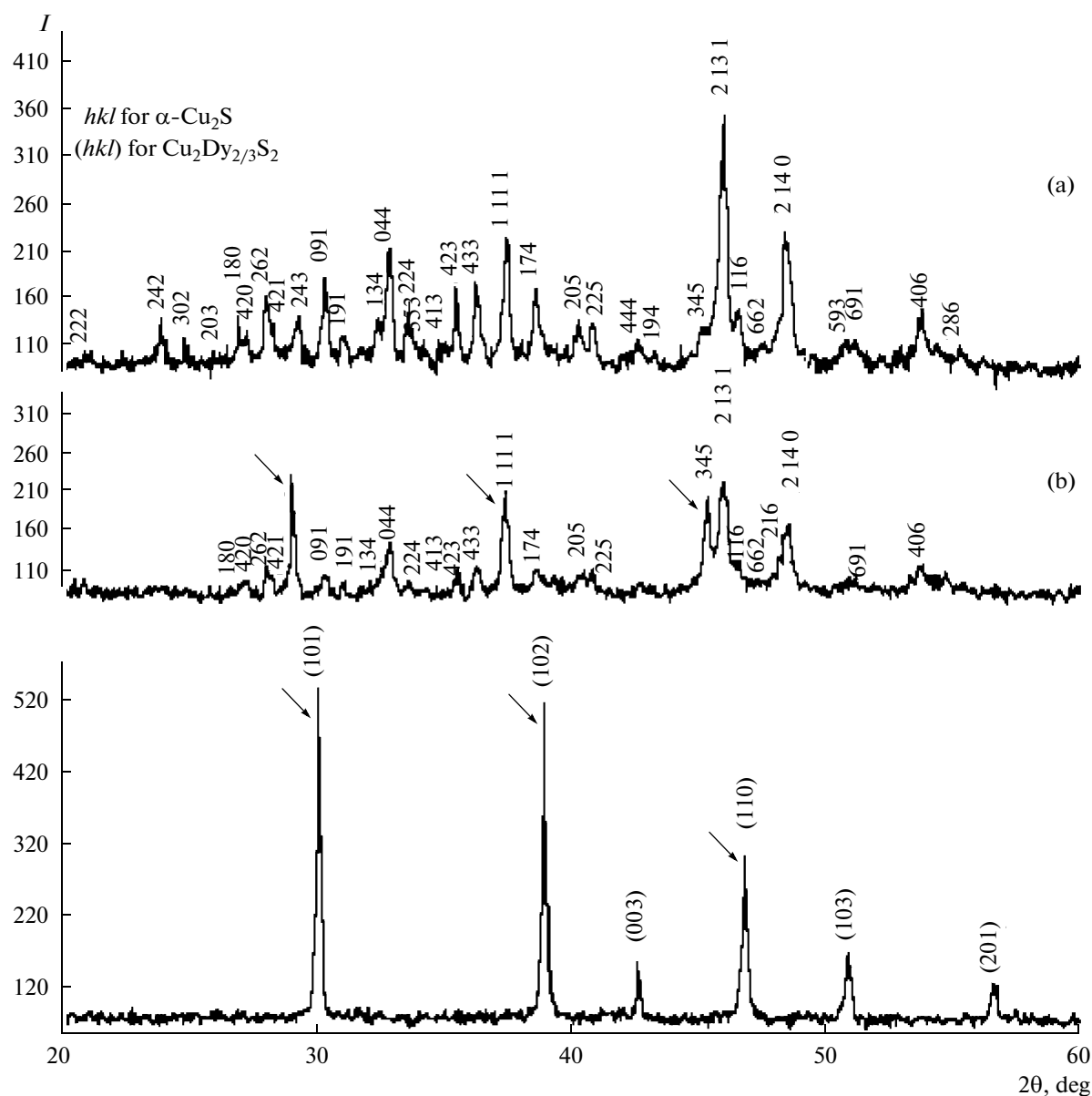
The extent of the Cu<sub>2</sub>S-base ss increases as temperature rises. According to MSA, a portion of the sample with 4.0 mol % EuS annealed at 770 K is homogeneous. The sample having 5.0 mol % EuS contains a small amount of acicular grains of the EuS phase having sizes of 5–30  $\mu$ m. The ss boundary at 770 K is set to lay 4.5 mol % EuS.

According to MSA, the samples annealed at 970 K and containing up to 7.0 mol % EuS are homogeneous ( $H = 950$  MPa) (Fig. 2). In the 8.0–13.0 mol % EuS samples, the Cu<sub>2</sub>S phase field is throughout penetrated by acicular inclusions of gray crystals of the conjugate EuS ss phase with lengths ranging from 2 to 30  $\mu$ m, sometimes up to 100  $\mu$ m, and 1–2  $\mu$ m wide. As the composition shifts, the content of the conjugate phase increases systematically. The shapes, sizes, and distribution character of EuS ss phase grains imply the solid-phase decomposition of the  $\beta$ -Cu<sub>2</sub>S primary solid solution.

As the EuS concentration in the solid solution increases, the kinetics of  $\beta$ -Cu<sub>2</sub>S ss  $\rightarrow$   $\alpha$ -Cu<sub>2</sub>S ss solid-phase transformations changes. The samples annealed

#### Balance equations of phase transformations in the Cu<sub>2</sub>S–EuS system

Phase transformation	Invariant point coordinates		Phase-transformation equation	$\Delta H_m$ , J/g
	composition, mol % EuS, T, K	T, K		
Peritectoid phase transition in a Cu <sub>2</sub> S-based ss	6.5	379	0.95 $\beta$ -Cu <sub>2</sub> S ss (0.015 EuS; 0.985 Cu <sub>2</sub> S) + 0.05 EuS ss (0.985 EuS; 0.015 Cu <sub>2</sub> S) $\leftrightarrow$ $\alpha$ -Cu <sub>2</sub> S ss (0.065 EuS; 0.935 Cu <sub>2</sub> S)	26
Eutectic melting in the Cu <sub>2</sub> S–EuS system	24.5	1069	0.89 $\beta$ -Cu <sub>2</sub> S ss (0.155 EuS; 0.845 Cu <sub>2</sub> S) + 0.11 EuS ss (0.945 EuS; 0.055 Cu <sub>2</sub> S) $\leftrightarrow$ L (0.245 EuS; 0.755 Cu <sub>2</sub> S)	38
Incongruent decomposition of $\beta$ -Cu <sub>2</sub> S-based ss	7.0	1186	$\beta$ -Cu <sub>2</sub> S ss (0.07 EuS; 0.93 Cu <sub>2</sub> S) $\leftrightarrow$ 0.72 $\gamma$ -Cu <sub>2</sub> S ss (0.035 EuS; 0.965 Cu <sub>2</sub> S) + 0.28 L (0.16 EuS; 0.84 Cu <sub>2</sub> S)	12



**Fig. 4.** X-ray diffraction patterns for portions of  $\text{Cu}_2\text{S}$ – $\text{EuS}$  samples annealed at 350 K for 3 years. Recording conditions: Ni-filtered  $\text{CuK}\alpha$  radiation. Panel (a): 1 mol %  $\text{EuS}$ . The phase composition of the sample:  $\alpha$ - $\text{Cu}_2\text{S}$ . Unit cell parameters:  $a = 1.3459$  nm,  $b = 2.7288$  nm,  $c = 1.1885$  nm. Panel (b): 6 mol %  $\text{EuS}$ . The phase composition of the sample:  $\beta$ - $\text{Cu}_2\text{S}$  +  $\alpha$ - $\text{Cu}_2\text{S}$ . Unit cell parameters: for  $\alpha$ - $\text{Cu}_2\text{S}$ :  $a = 1.3476$  nm,  $b = 2.7287$  nm,  $c = 1.1864$  nm; for  $\beta$ - $\text{Cu}_2\text{S}$ :  $a = 0.3962$  nm,  $c = 0.6739$  nm. The arrow marks reflections from the structural motif of a  $\text{Cu}_2\text{Ln}_{2/3}\text{S}_2$ -type phase.

at 970 K and quenched feature reflections from the following phases:  $\alpha$ - $\text{Cu}_2\text{S}$ -based and  $\beta$ - $\text{Cu}_2\text{S}$ -based ss (1.0–12.0 mol %  $\text{EuS}$ ) with a systematic increase in  $\beta$ - $\text{Cu}_2\text{S}$  concentration;  $\beta$ - $\text{Cu}_2\text{S}$ -based ss and  $\text{EuS}$ -based ss (15.0–94.0 mol %  $\text{EuS}$ ). Within the extent of the solid solution, there is a scatter in the variation in  $\text{Cu}_2\text{S}$  unit cell parameter depending on the composition.

Phase equilibria in the system are proven by the microhardness–composition curve (Fig. 2). The microhardness of  $\alpha$ - $\text{Cu}_2\text{S}$  crystals is 1590 MPa and decreases to 740 MPa within the ss region. The survival of  $\beta$ - $\text{Cu}_2\text{S}$ -based ss upon quenching from 970 K allowed us to measure its microhardness for the first

time; the microhardness decreases to 950 MPa as the  $\text{EuS}$  concentration increases.

The extent of  $\gamma$ - $\text{Cu}_2\text{S}$ -based ss was derived from DSC data. The  $\gamma$ - $\text{Cu}_2\text{S}$ -based ss has a closed type field; at 1186 K  $\gamma$ - $\text{Cu}_2\text{S}$  dissolves 3.5 mol %  $\text{EuS}$ .

The solidus–liquidus portion of the phase diagram was constructed proceeding from DSC data. Weight loss was not observed upon heat treatments. In samples containing 1.0, 2.0, or 3.0 mol %  $\text{EuS}$ , there is a peak of an extended shape, which is characteristic of monovariant melting of samples from the ss region. The onset temperatures (1366, 1325, and 1310 K; the

solidus line) and end temperatures (1400, 1391, and 1388 K; the liquidus line) of heat absorption were fitted by a second-order polynomial. Thermoanalytical curves for portion of samples containing 4.0, 5.0, 6.0, or 7.0 mol % EuS each feature two peaks (Fig. 2). The first peak has a well-defined linear segment, indicating that invariant equilibrium in the phase diagram corresponds to this phase transformation. The second peak appears over a temperature range and is characteristic of melting of primary separated crystals. The appearance temperature of the peak having a linear segment averaged over 12 samples is (1186 ± 3) K. Tammann's triangle construction shows that a maximal peak area appears in the sample that contains 7.0 mol % EuS. The heat effect for the sample of this composition is 12 J/g (table). This peak is due to the invariant phase transformation, namely, the incongruent melting reaction of the β-Cu<sub>2</sub>S-based ss. The tie-line corresponding to this reaction is positioned in a concentration range of 3.5–16.0 mol % EuS. The balance equation of the phase transformation was compiled (table).

DSC curves for portions of 8.0–15.0 mol % EuS samples feature solidus temperatures between peritectic and eutectic temperatures. At 1069 K, the solubility of EuS in β-Cu<sub>2</sub>S was set equal to 15.5 mol % EuS. The β-Cu<sub>2</sub>S-based ss field has a polygonal shape; the solid solubility is temperature dependent and exsolution is incongruent.

A eutectic is formed between the β-Cu<sub>2</sub>S ss and EuS ss phases in samples containing 16.0–94.0 mol % EuS; the average eutectic temperature is (1069 ± 2) K. The eutectic composition derived from Tammann's triangle construction and MSA data is 24.5 mol % EuS. The heat of eutectic melting according to DSC is 38 J/g (table).

On polished sections, the eutectic mixture is represented by an alternation of elongated Cu<sub>2</sub>S crystals and more rounded, well-formed EuS crystals having sizes of 10–20 μm (Fig. 3).

Melting of primary EuS crystals is not detected by DSC, although melting of samples is observed visually. The eutectic–EuS branch of the liquidus line was constructed using VPTA data (Fig. 1); a negative nonlinearity is observed. The Cu<sub>2</sub>S–eutectic portion of the liquidus line is comprised of two branches, which were constructed by fitting DSC data to second-order polynomials using the Edstate 2D program.

There is a EuS-based ss field (Fig. 1). Within the homogeneity range, the EuS unit cell parameter decreases from  $a = 0.5967$  nm to  $a = 0.5955$  nm at 1770 K and  $a = 0.5959$  nm at 970 K. The solidus point position (93.0 mol % EuS (at 1770 K) and 95.0 mol % EuS (1170 K)) and the solvus point position (95.0 mol % EuS (at 970 K) and 97.0 mol % EuS (770 K)) were derived from the temperature-dependent variation of the unit cell parameter and the appearance of a second phase in the samples.

The heat of solution of EuS in β-Cu<sub>2</sub>S was estimated from the solvus line position using the Schroeder–Le Chatelier's equation [10] in the form

$$\frac{1}{T} = A + B \ln x^S, \quad (1)$$

where  $x$  is the EuS mole fraction and  $T$  is the EuS dissolution temperature in β-Cu<sub>2</sub>S, in degrees Kelvin.

The solvus curve, which bounds the β-Cu<sub>2</sub>S ss field in the Cu<sub>2</sub>S–EuS system, is well fitted by model (1): the correlation factor  $r = 0.88$ , and the heat of dissolution calculated from  $\Delta_s H = -\frac{R}{B}$ , is 11.87 kJ/mol, where  $R$  is the universal gas constant, equal to 8.31 J/(mol K). The thermodynamic assessment of the nonideality of behavior of EuS dissolved in β-Cu<sub>2</sub>S is carried out using the equation [10]:

$$\bar{G}^E = \Delta_s H(AT - 1) - RT \ln x^S. \quad (2)$$

The calculated values show a considerable positive nonideality for a β-Cu<sub>2</sub>S ss, indicating the nonexistence of intermediate phase formation in the system.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. V. G. Bamburov and O. V. Andreev, *Russ. J. Inorg. Chem.* **47**, 598 (2002).
2. *Binary Metal Phase Diagrams: A Handbook*, Ed. by N. P. Lyakishev (Mashinostroenie, Moscow, 1997) [in Russian].
3. O. A. Sadovskaya, A. A. Eliseev, and N. M. Ponomarev, *Refractory Compounds of the Rare-Earth Elements* (Donish, Dushanbe, 1978) [in Russian].
4. O. V. Andreev, Doctoral Dissertation in Chemistry (Tyumen, 1999).
5. W. Cook, L. Shiozawa, and F. Augustine, *J. Appl. Phys.* **41**, 3058 (1970).
6. O. Andreev, *Russ. J. Inorg. Chem.* **34**, 909 (1989).
7. O. V. Andreev, *Zh. Neorg. Khim.* **38**, 687 (1993).
8. A. V. Ruseikina, A. S. Zalineeva, and O. V. Andreev, in *Physicochemical Analysis of Natural and Technical Systems: Collected Works* (Tyumen, 2008), p. 159 [in Russian].
9. R. Ballestracci and E. F. Bertaut, *Bull. Soc. Franc. Miner. Crist.* **88**, 575 (1965).
10. N. A. Khritokhin, O. V. Andreev, A. S. Korotkov, and O. Yu. Mitroshin, *Proceedings of the 1st All-Russian Conference “Physicochemical Processes in Condensed Matter and at Interfaces,” Voronezh, 2002* (Voronezh State Univ., Voronezh, 2002), p. 369 [in Russian].
11. A. V. Ruseikina, O. V. Andreev, and N. A. Khritokhin, *Proceedings of the 17th International Conference on Chemical Thermodynamics in Russia, Kazan, 2009* (Kazan, 2009), Vol. 2, p. 306 [in Russian].