*Research Article*

# Electron Transport Properties of Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ ($0 \leq x \leq 1$): Initiation of Transition Eu$^{2+}$ $\leftrightarrow$ Eu$^{2.41+}$ in the Intermediate Valence State

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The article presents the results of studies of the chemical composition, crystal structure, lattice parameters, microstructure, the valence state of the europium ion (at 300 K), electrical resistivity, and differential thermopower (6–400 K) of samples in the Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ ($0 \leq x \leq 1$) substitutional solid solutions. A transition of the europium ion from the valence-stable state of Eu$^{2+}$ in EuAg$_2$Si$_2$ to the state of intermediate (homogeneous) valence (IV) of the europium ion in EuCu$_2$Si$_2$ with an effective valence $\vartheta_{\text{eff}} = 2.41$ (300 K) has been initiated by a successive replacement of silver atoms by copper atoms. With appropriate sample compositions, the transition passes through a Kondo-type state. The research subject is the patterns of transformations (when the composition of the sample changes), the electronic state, and, accordingly, the electronic transport properties. The simultaneous coexistence of europium ions in different electronic states is assumed. The substitutional solid solution Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ ($0 \leq x \leq 1$) exhibits properties related to the competition between the state of the Kondo system, intermediate valence (IV), and magnetic ordering.

## 1. Introduction

Intermetallic compounds with strongly correlated electronic properties have caused and caused extreme interest in researchers. Several theoretical descriptions concerning the highly correlated nature of 4$f$-elements in these systems are distinguished as systems with intermediate (homogeneous mixed) valence, heavy fermions, and a Kondo lattice. The physical mechanism of the occurrence of the abovementioned phenomena in the materials united by the general name of strongly correlated electronic systems is the object of study up till today.

Depending on the magnitude of the correlation energy of localized–delocalized electrons, they undergo spin fluctuations and/or charge fluctuations. The connection between $f$- and conduction electrons ($s$- and $d$-type) depends on the energy closeness of the $f$-level to the Fermi surface $E_F$ and determines the unusual physical properties of the described materials. Most of the known

materials with strong electron–electron correlations are synthesized based on 4$f$- or 5$f$-elements (Ce, Eu, Yb, U), in which a well-localized $f$-shell can have a local magnetic moment. In this case, you can expect the manifestation of Kondo properties. At the same time, the interaction of $f$-electrons with the conduction band tends to the appearance of long-range magnetic order due to the Ruderman–Kittel–Kasuya–Yosida (RKKY) indirect mechanism.

Until now accumulated information indicates that for Eu in metallic crystals, there are possible stable states of Eu$^{2+}$, ($4f^7$, ground state $^8S_{7/2}$, with magnetic moment $\mu_{\text{eff}} = 7.9\,\mu_B$), Eu$^{3+}$ ($4f^6$, ground state $^7F_0$, nonmagnetic), and the state of intermediate (dynamic, homogeneous) valence $4f^7 \leftrightarrow 4f^6$ (in other terminology—the state of interconfigurational fluctuations (ICF). It is established in the ICF model, that the rare-earth ion achieves its state of intermediate valence due to a rapid fluctuation (with a frequency of the order of $10^{12}s^{-1}$) between

two ionic configurations $4f_o^{n+1}$ and $4f_o^n$ + fr.e. (fr.e.—free electron). The two configurations are separated by the excitation energy $\varepsilon_{ex}$. As mentioned above, in the case when one of the states is magnetic, and the other is nonmagnetic, then the process can occur simultaneously with the mechanism of indirect RKKY interaction (magnetic ordering), while Kondo interactions can cancel out the long-range magnetic order.

The ICF state, like all phenomena associated with the term of strong electron–electron correlations, is of particular interest to the physics of metals. In this case, a radical restructuring of the electronic state of the crystal takes place in the form of the emergence of resonant electronic states of different amplitudes in the electronic spectrum of the metal matrix. The consequence of this is a change in macroscopic physical properties, which is easily observed using a large number of experimental methods.

Except the ICF state, for Eu was also predicted to display the properties of the Kondo system [1–3]. The phenomena of the Kondo system were widely observed for dilute and concentrated (concerning RE atoms) compounds based on cerium, europium, and ytterbium, in particular, discussed in the paper [4]. Theoretical estimates of the conditions for the manifestation of the Kondo effect in a metallic matrix with Eu are described in [1].

As regards europium compounds belonging to the widely used isostructural ternary compounds of the $RM_2X_2$ type (structural type $CeAl_2Ga_2$ ($ThCr_2Si_2$), extension to $BaAl_4$), the studied systems are often based on the known ternary compounds $EuCu_2Si_2$ and $EuPd_2Si_2$, $EuAg_2Si_2$ and on solid substitutional solutions based on them. The results of their research are presented in a number of our works [2, 5–7] and a huge number of works devoted to research in this interesting section of solid-state physics.

Let us single out the study of the solid solution of $EuCu_{2-y}Ag_ySi_2$ substitution, conducted by Görlich et al. [8, 9] using the method of Mössbauer spectroscopy. The conclusion about the special nature of the magnetic ordering in the samples of this system is interesting.

The proposed work presents the original experimental results of the study of the influence of intersubstitution of components in the sublattice of a transition metal on the microstructure (taking into account the conclusions of Görlich et al.'s [8, 9] study), electron-transport properties, and effective valence of europium in a quasiternary solid solution of $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) substitution.

The peculiarity of this solid solution is that both of its components, $EuAg_2Si_2$ and $EuCu_2Si_2$, have significant regions of homogeneity (from the point of view of belonging to the same crystal structure, i.e., single phase). The work was carried out in the context of consideration of the question: how does the nature of the transition (stable europium ion—the state of ICF) correlate with the state of magnetic ordering, Kondo-type state, or the state of intermediate valence in compounds of this class.

## 2. Experimental Procedure

High-purity components Eu—99.81%, Cu, Ag, and Si—99.999% were used for the synthesis of alloys. Alloys were synthesized by direct fusion of components in an electric arc-melting furnace on a water-flowing copper base, in an atmosphere of high purity argon, at a pressure of $1 \cdot 10^5$ Pa, using Ti as a getter and a tungsten electrode, and followed by homogenizing annealing at 700 K for 250 hr.

Microscopic studies were carried out using an electronic scanning electron microscope REMMA-102. Photomicrographs were obtained in composite mode (COMPO) in back-scattered electrons, which allows identification of the phase composition of the samples.

The elemental composition of individual phases was obtained using an energy-dispersive X-ray spectroanalyzer (EDS).

The alloy crystal structure was studied using an X-ray diffractometer DRON-2.0M ($FeK_\alpha$ radiation). The Eu valence state was investigated by means of X-ray $EuL_{III}$-absorption spectroscopy at $T = 300$ K.

Temperature dependences (in the range of 6–400 K) of resistivity and differential thermopower were obtained by standard methods (in particular, the two-probe method on direct current for resistance).

Magnetoresistance in fields up to 13 T and a temperature range of 5–300 K was investigated on the equipment of the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland).

## 3. Results and Discussion

*3.1. Structural Properties.* The $Eu(Ag_xCu_{1-x})_2Si_2$ system can be considered as a quasiternary solution of two ternary compounds $EuAg_2Si_2$ and $EuCu_2Si_2$ (both crystallize in the structural type $CeAl_2Ga_2$). It is known [7] that in $EuAg_2Si_2$, the europium ion is stable $Eu^{2+}$, while in $EuCu_2Si_2$, the ion europium is in a state of homogeneous intermediate valency with $\vartheta_{eff} = 2.41$ (300 K) [2]. Evidently, in the case of the existence of a quasiternary solid solution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$), we would have an opportunity to observe the nature of the transition of europium from one state to another. Unlike the similar system $Eu(Ag_xCo_{1-x})_2Si_2$ ($0 \leq x \leq 1$), for which it has not been possible to obtain single-phase alloys from the point of view of the crystal structure [10], in the system $Eu(Cu_{1-x}Ag_x)_2Si_2$, the existence of a continuous solid solution has been indeed discovered in the whole interval $0 \leq x \leq 1$. Alloys of all compositions are unambiguously identified as single-phase and crystallized with a structure of the $CeGa_2Al_2$ type, where Eu ions occupy tetragonally coordinated nodes with 4/mmm symmetry (in ordered pure ($x = 0$ or $x = 1$) compounds). Note that it was in this type of Eu compound, in the compound $EuCu_2Si_2$, the presence of charge fluctuations in the $f$ shell was detected for the first time using Mössbauer spectroscopy of $^{151}$Eu nuclei. The existence of a strong temperature dependence of the isomeric shift is explained by a change in the effective valence of Eu from 2.8 ($T = 4.2$ K) to 2.4 ($T = 600$ K) [11]. The effective valence of europium in the region of homogeneity $EuCu_{2.25-1.25}Si_{1.75-2.75}$ was studied by the $L_{III}$-absorption spectroscopy method in [12]. Conclusions from the work [9] regarding the nature of the formation of magnetic order in $EuCu_{2-y}Ag_ySi_2$ (identical notation $Eu(Cu_{1-x}Ag_x)_2Si_2$

1-EuCu$_2$Si$_2$



5-Eu(Cu$_{0.50}$Ag$_{0.50}$)$_2$Si$_2$



2-Eu(Cu$_{0.95}$Ag$_{0.05}$)$_2$Si$_2$



6-Eu(Cu$_{0.25}$Ag$_{0.75}$)$_2$Si$_2$



3-Eu(Cu$_{0.875}$Ag$_{0.125}$)$_2$Si$_2$



7-Eu (Cu$_{0.125}$Ag$_{0.875}$)$_2$Si$_2$
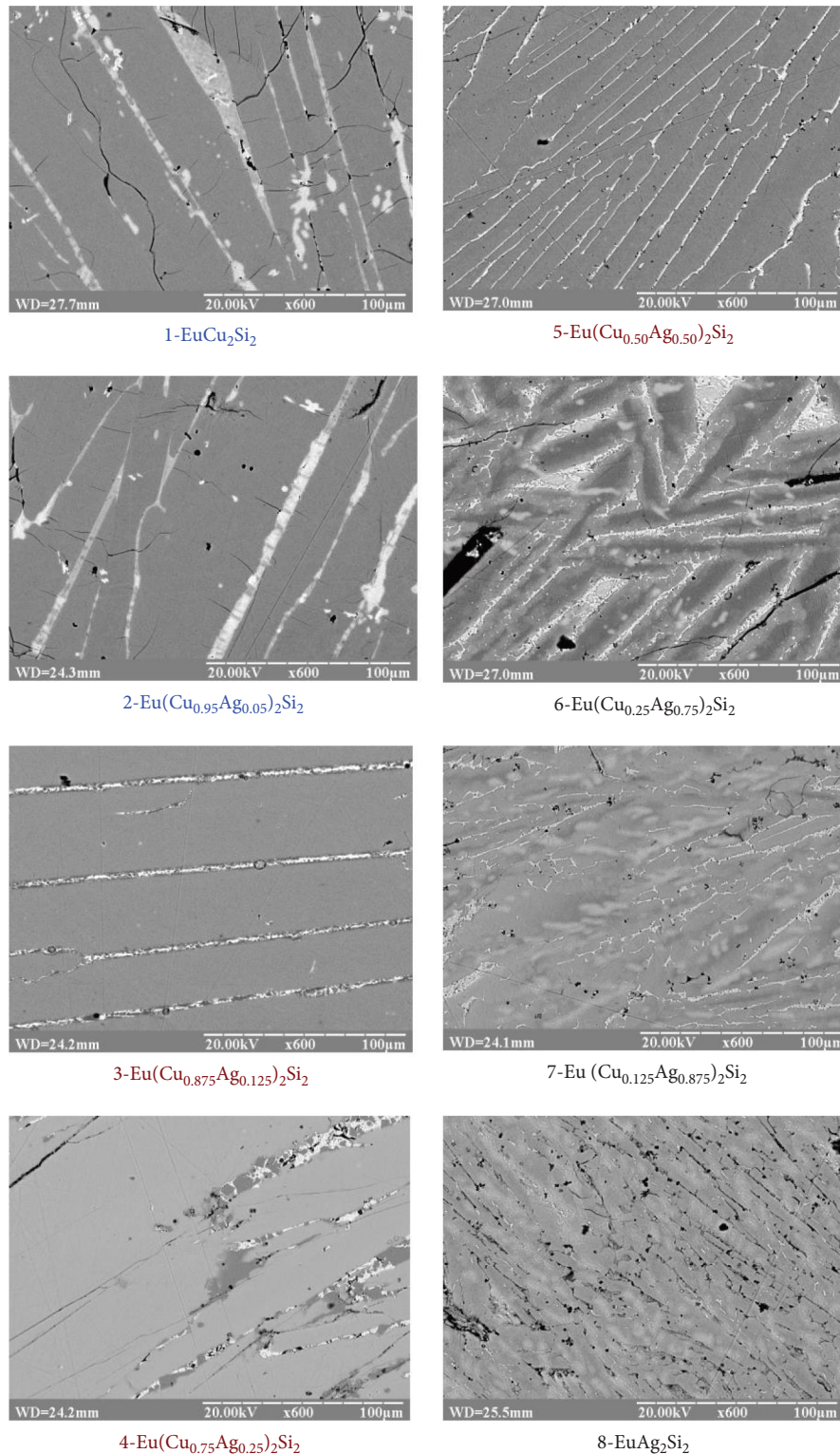


4-Eu(Cu$_{0.75}$Ag$_{0.25}$)$_2$Si$_2$



8-EuAg$_2$Si$_2$

FIGURE 1: Microstructure of Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ alloys (magnification 600). Investigating was performed using a scanning electron microscope REMMA-102-02 (also, the quantitative and qualitative analysis of a composition). *Note.* The color coding of the number and composition of the samples assigns them to certain groups and will reveal itself as the article progresses.

$(0 \le x \le 1)$) prompted us to more carefully consider the features of crystal formation in this substitutional solid solution. It is important to establish a causal relationship between the features of crystal formation and physical properties (kinetic, magnetic).

Let us start with the microstructure of Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ $(0 \le x \le 1)$. In Figure 1, photographs of the surface (microstructure, magnification ×600) of alloys of different compositions obtained with the help of an electron scanning
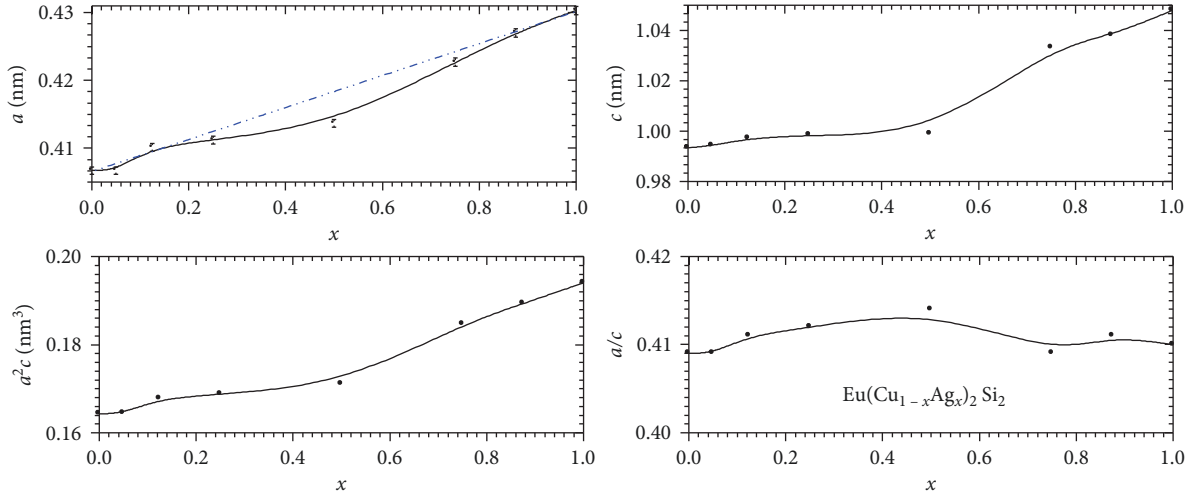
FIGURE 2: Composition dependence of the lattice parameter of $Eu(Cu_{1-x}Ag_x)_2Si_2$ alloys. The maximum error in determining $a$ and $c$ does not exceed $\pm 0.0006$ nm in all cases: solid line—B-spline and blue dash dot line—direct line.

microscope are presented. The characteristic feature is the transition from a fine crystal structure in alloys that are closer in composition to $EuAg_2Si_2$ to larger crystallites elongated in one direction in alloys that are closer in composition to $EuCu_2Si_2$.

The second feature of crystal formation in $Eu(Cu_{1-x}Ag_x)_2Si_2$ $(0 \leq x \leq 1)$ is the presence of heterogeneity in composition within individual grains (crystallites). This is manifested in the images of the sample surface by lighter or darker areas when scanning the sample surface by the BSE (COMPO-regime) method (Figure 1).

To distinguish them, we will call them "macroheterogeneity" in contrast to the term "microheterogeneity," which describes the qualitative composition within the unit cell, that is, in the immediate environment of the europium atom. Lighter regions correspond to a bigger number of heavy elements. If the composition of the alloy is determined as an integral value from an area of $200 \, \mu m \times 200 \, \mu m$, then it agrees well with the calculated composition of the alloy, depending on charge weights before fusion.

Alloy sample labeling corresponds to the calculated composition (coincides with the integral value of the composition determined by the energy dispersive X-ray spectroanalyzer (EDS) method).

The observed "macroheterogeneity" within individual crystallites decreases in number (quantity) and increases in size when the composition changes from $EuAg_2Si_2$ to $EuCu_2Si_2$, up to a complete visual fusion. In $EuCu_2Si_2$, the indicated "heterogeneity" is practically not observed.

They are also absent in most of the $EuM_2X_2$ type compounds (M = $d$-element, $X$ = Ge, Si) and solid solutions based on them.

We can assume that this is a property of this solid solution, which may be possible (among other reasons) due to the presence of a significant area of homogeneity of the components of this substitutional solid solution, namely $EuCu_{2.25-1.25}Si_{1.75-2.75}$ i $EuAg_{2.00-1.25}Si_{2.00-2.75}$ [5, 7].

In addition to "macroheterogeneity" in composition within individual crystallites, silver enrichment of the alloy volume between individual crystallites (intercrystalline phase) is observed in all samples, including $EuAg_2Si_2$. This may indicate a possible replacement of silver with silicon already at the microlevel (compared to the calculated composition of the alloy). An excess of silicon in this type of alloy leads to the stabilization of the divalent state of europium, which we will discuss below.

Therefore, we conclude that, most likely, when producing alloys in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ $(0 \leq x \leq 1)$ system, a change in the silver–copper ratio leads to both monotonous spatial segregation of elements in the alloys, and the formation of "macroinhomogeneities" in composition within individual crystallites.

Without emphasizing the absolute values in determining the composition of individual regions of the alloy, we will try to determine the nature of changes in physical properties during the successive replacement of silver atoms by copper atoms when obtaining these alloys. The increase in the size of crystallites occurs against the background of compression of the crystal lattice (Figure 2).

The tetragonal lattice is compressed in both parameters when replacing silver with copper. The rate of decrease of the latter slows down at $x = 0.5$. Accordingly, the compositional dependence of the unit cell volume has the same qualitative character as the "$c$." Although the deviations from Vegard's law are not so significant, we nevertheless maintain that Vegard's law is not fulfilled. As mentioned above, the symmetry of the crystal lattice (in the first approximation) is preserved.

*3.2. X-Ray $L_{III}$-Absorption Spectroscopy and Effective Valence of Europium.* The effective valence of europium was determined using X-ray $L_{III}$-absorption spectroscopy experiments. X-ray $L_{III}$-absorption spectra of Eu in $EuAg_{2.00-1.25}Si_{2.00-2.75}$ have one maximum [7], which corresponds to $Eu^{2+}$ in energy. When "$x$" decreases ($x < 0.75$) in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ $(0 \leq x \leq 1)$
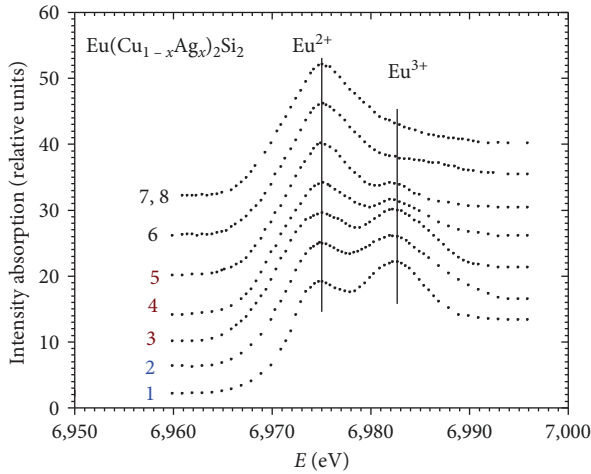
FIGURE 3: X-ray Eu$L_{III}$-absorption spectra of Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ alloys at $T = 300$ K, $x = 0.0$ (1), 0.05 (2), 0.125 (3), 0.25 (4), 0.50 (5), 0.75 (6), 0.875 (7), and 1 (8). 1-EuCu$_2$Si$_2$, 2-Eu(Cu$_{0.95}$Ag$_{0.05}$)$_2$Si$_2$, 3-Eu(Cu$_{0.875}$Ag$_{0.125}$)$_2$Si$_2$, 4-Eu(Cu$_{0.75}$Ag$_{0.25}$)$_2$Si$_2$, 5-Eu(Cu$_{0.50}$Ag$_{0.50}$)$_2$Si$_2$, 6-Eu(Cu$_{0.25}$Ag$_{0.75}$)$_2$Si$_2$, 7-Eu(Cu$_{0.125}$Ag$_{0.875}$)$_2$Si$_2$, and 8-EuAg$_2$Si$_2$.



FIGURE 4: Composition dependence of the effective valence $\vartheta_{eff}$ of europium in Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ alloys at $T = 300$ K: 1—according to Eu$L_{III}$-absorption spectra, black solid line—B-spline; 2—according to isomeric shift, Mössbauer effect, red solid line—B-spline [8, 9].



FIGURE 5: The effective valence of Eu ion (probability $p_{3+}$ presence in Eu$^{3+}$ state) depending on the excitation energy, for different temperatures, is calculated in the frame of the ionic model of interconfigurational fluctuations [11].

system a second peak in the range of energies characteristic of Eu$^{3+}$ appears in the spectrum (Figure 3).

The effective valence of europium, calculated from the ratio of absorption intensities, shows that the "chemical compression" of the crystal lattice ($x < 0.75$) leads to the transition of the europium ion from the Eu$^{2+}$ state to the state with $\vartheta_{eff} = 2.41 \pm 0.03$ (300 K) ($x = 0$) (Figure 4) [13].

The nature of the transition correlates with similar data on the effective valence obtained using the Mössbauer effect [8] and the nature of the change in the parameters of the crystal lattice. An interesting fact is that according to the data on the isomer shift in the Mössbauer effect, the effective valence of europium is different from Eu$^{2+}$ already at the composition $x = 0.875$ [8], while according to our data from X-ray $L_{III}$-absorption spectroscopy, the effective valence of europium at $x = 0.75$ is still equal to Eu$^{2+}$ and begins to increase only with further substitution of silver for copper (Figure 4). The discrepancy between the absolute values of the effective valence of europium, obtained using the Mössbauer effect and X-ray $L_{III}$-absorption spectroscopy, was discussed in the literature, in particular in [14]. We do not focus on this, since in this case, same as before, we are more interested in trends and not in absolute values.

As you can see, the replacement of silver with copper, which initiates "chemical compression" of the crystal lattice, leads to a rearrangement of the electronic structure of the crystal. According to the ion model of ICF [11], in [2], we calculated the effective valence of europium as a function of temperature for different values of the excitation energy. Assuming that in our case, a change in the composition of the sample leads to a mode of ICF, that is, to a change in the excitation energy, we will provide a graph of the effective valence of the europium ion as a function of the actual excitation energy for different temperatures (Figure 5).

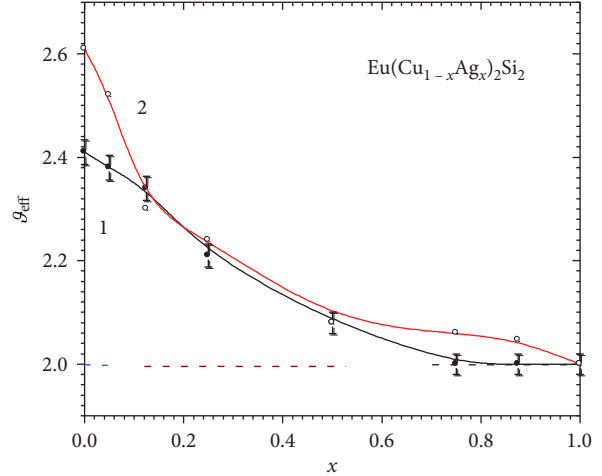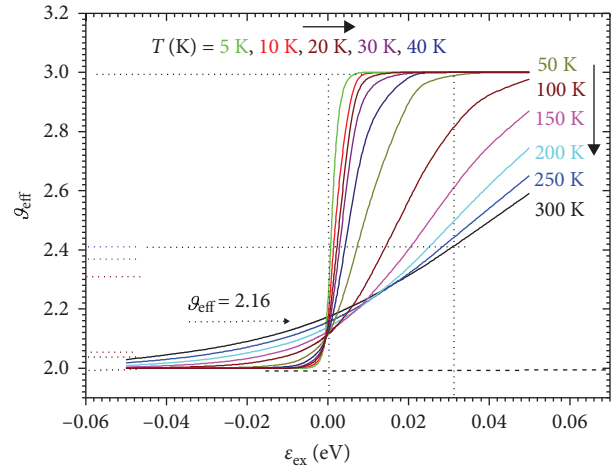In some of our previous works [15, 16], we assumed, that under certain conditions, there can be existence and coexistence of intermediate valence states, Kondo states, and states of magnetic ordering in compounds and solid solutions of substitution of the same type as Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$. Thus, with an effective valence greater than 2.35, the existence of the Kondo state is unlikely. At the same time, with an effective valence of around 2.16, the Kondo state may actually become dominant. At lower values, competition between the Kondo state and magnetic ordering can occur up to the region of complete dominance of one of these states. Again, we caution that these values may differ for each system.

Figure 5 is designed to "visualize" (predict) a possible cause-and-effect relationship in the chain of composition—excitation energy, valence of the europium ion (i.e. electronic structure)—kinetic and magnetic properties.

When the symmetry of the crystal lattice is preserved, the characteristic change in the symmetry of the valence
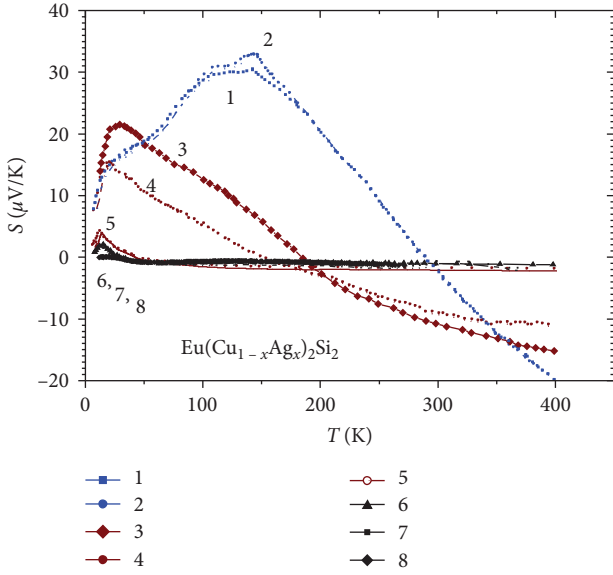
FIGURE 6: Temperature dependences of thermopower for Eu(Cu$_{1-x}$Ag$_x$)$_2$ Si$_2$ alloys: $x = 0.0$ (1), 0.05 (2), 0.125 (3), 0.25 (4), 0.50 (5), 0.75 (6), 0.875 (7), and 1 (8). Solid line—B-spline.



FIGURE 7: Temperature dependences of reduced resistivity of Eu (Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ alloys: $x = 0$ (1), 0.05 (2), 0.125 (3), 0.25 (4), 0.50 (5), 0.75 (6), 0.875 (7), and 1 (8). Solid line—B-spline.

fluctuations when the composition of the system changes implies a corresponding transformation of the electron transport and magnetic properties of the crystal.

*3.3. Electronic Transport.* Temperature dependences of the thermopower and electrical resistance Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ ($0 \leq x \leq 1$) are presented in Figures 6 and 7, respectively. Data on electrical resistance are presented in the normalized form to exclude measurement errors of geometric dimensions, as well as errors associated with some imperfection of samples obtained by the method of arc melting.

Temperature dependences of the thermopower and electrical resistance are characterized by "low" and "high-temperature" features (maximums or minimums), which can be associated with the presence of the europium ion in the IV state or the Kondo state. With a change in the composition of the sample, the specified features undergo a certain transformation.

Based on the temperature dependence of electron transport properties, the studied Eu(Cu$_{1-x}$Ag$_x$)$_2$Si$_2$ ($0 \leq x \leq 1$) alloys can be conditionally divided into a few groups.

We highlight the groups by color. We have already done this in Figures 6 and 7, same as we did earlier in the text, grouping samples by certain characteristics. This was announced in the caption of Figure 1.

The sample with the limiting value of $x = 1$ (EuAg$_2$Si$_2$) is characterized by the absence of anomalies in the temperature dependences of the thermopower and electrical resistance. For thermopower, this is the usual diffusion thermopower with small negative values and almost linear temperature dependence. The temperature dependence of electrical resistance has a classic metallic character—it is a linear temperature dependence with a tendency to saturation at $T \rightarrow 6$ K ("residual" resistance). We denote "residual" resistance, since it is not yet a true residual resistance. It is described by the
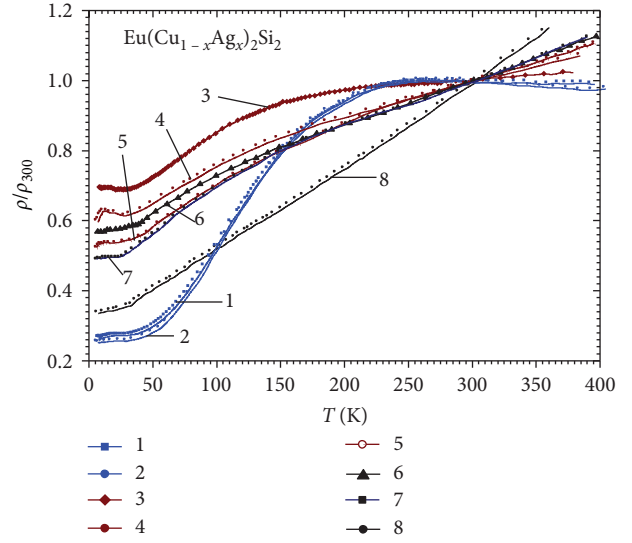
Bloch–Grüneisen formula (Bloch–Grüneisen law) same as in the case of the isostructural analog LaCu$_2$Si$_2$ [15, 16].

In the compositional interval from $0.50 \leq x \leq 0.875$, the gradual replacement of silver atoms by copper atoms leads to the detection of a low-temperature thermopower peak, which increases in absolute value with decreasing of "$x$" at a constant temperature of its location around 13 K. The temperature of the transition of thermopower from negative to positive values shifts toward higher temperatures.

Temperature dependences of electrical resistance in the composition interval are characterized by a nonlinear dependence and high "residual" resistance values at $T \rightarrow 6$ K.

In the compositional interval $0.125 \leq x \leq 0.25$, when "$x$" is reduced (replacement of silver in the middle), the low-temperature peak on the temperature dependency of thermopower further increases in absolute value to $20 \mu$V/K, and a characteristic influx (second maximum) appears on the curve at slightly higher temperatures. The temperature of the transition of thermopower from negative to positive values increases again. The temperature dependence of electrical resistance has an even more pronounced nonlinear character. At $T \rightarrow 6$ K, the "residual" resistance is relatively large. On the background of the overall increase in electrical resistance a low-temperature maximum appears.

In the compositional interval $0.0 \leq x \leq 0.05$, the temperature dependences of thermopower and electrical resistance exhibit the same behavior as EuCu$_2$Si$_2$. There is a high-temperature maximum around 124 K on the temperature dependence of the thermoelectric power and a relatively small peculiatity in the low-temperature region (10–20 K). The temperature dependence of electrical resistance has a significantly nonlinear character, and the residual resistance at $T \rightarrow 6$ K has small absolute values. It is logical that the nature of some temperature dependences of thermopower and electrical resistance can be considered as the coexistence of low-temperature and high-temperature features.

TABLE 1: Parameters of temperature dependences of thermopower and resistivity in the system $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$).

| Composition | $T^{\alpha}_{max}$ (K) | $\alpha_{max}$ ($\mu$V/K) | $T_{-/+}$ (K) | $\rho_{300}$ ($\mu\Omega\cdot$cm) | $\rho_{6\,K}/\rho_{300\,K}$ | $\vartheta_{eff}$ |
|---|---|---|---|---|---|---|
| 1-$EuCu_2Si_2$ | 142 | 30.3 | 300 | 260 | 0.24 | 2.41 |
| 2-$Eu(Cu_{0.95}Ag_{0.05})_2Si_2$ | 142 | 33.0 | 300 | 270 | 0.24 | 2.38 |
| 3-$Eu(Cu_{0.875}Ag_{0.125})_2Si_2$ | 28.0 | 21.5 | 183 | 139.12 | 0.70 | 2.34 |
| 4-$Eu(Cu_{0.75}Ag_{0.25})_2Si_2$ | 20.7 | 15.4 | 146 | 71.83 | 0.62 | 2.21 |
| 5-$Eu(Cu_{0.50}Ag_{0..50})_2Si_2$ | 13.5 | 4.28 | 46 | 56.28 | 0.54 | 2.08 |
| 6-$Eu(Cu_{0.25}Ag_{0.75})_2Si_2$ | 13.5 | 2.6 | 32 | 42.08 | 0.57 | 2.00 |
| 7-$Eu(Cu_{0.125}Ag_{0.875})_2Si_2$ | 13.5 | 1.4 | 25 | 32.80 | 0.49 | 2.00 |
| 8-$EuAg_2Si_2$ | — | — | — | 33.30 | 0.34 | 2.00 |

$T^{\alpha}_{max}$, the temperature of the maximum thermopower $\alpha_{max}$; $\alpha_{max}$, the value of $\alpha_{max}$; $T_{-/+}$, the temperature of the thermopower transition from negative to positive values; $\rho_{300}$, the value of $\rho$ at 300 K; $\rho 6\,K/\rho 300\,K$, the ratio of the value of the resistivity at 6 K and 300 K; and $\vartheta_{eff}$, the effective valence of europium according to X-ray $L_{III}$-absorption spectroscopy data.

It is worth comparing the obtained observations with similar ones in similar compounds and solid solutions. In particular, in the solid solution of the $EuCu_2(Si_xGe_{1-x})_2$ substitution, when going from $EuCu_2Ge_2$ to $EuCu_2Si_2$, the resistivity changes as follows: in [14], the temperature dependences of electrical resistance change from the classical metallic type to the presence of a maximum on the temperature dependence curve at 15 K, while in [3], it was shown that already in $EuCu_2Ge_2$, there is a slight maximum and with a further decrease in temperature, a decrease in electrical resistance is observed (as can be the case with magnetic ordering or as in the case of concentrated Kondo systems).

The maximum initially increases in absolute value at a constant temperature, and later the dependence transforms into a curve with a high-temperature maximum. This maximum is shifted toward higher temperatures. The coexistence of two maximums of thermoelectric power in $EuCu_2(Si_xGe_{1-x})_2$ is observed in the range of compositions ($0.7 < x < 0.9$). In $EuCu_{2-x}Si_{2+x}$, the coexistence of two thermoelectrical maximums was observed for the composition $EuCu_{1.95}Si_{2.05}$ [5]. A similar coexistence is observed in $EuPd_{2-x}Si_{2+x}$ ($x = 0$, $-01$, $-0.2$) [6], $Lu_xEu_{1-x}Cu_2Si_2$ ($x = 0.2$, $0.3$) [15, 16]. Note that we use the term "coexistence of low-temperature maxima with high-temperature maxima," only in the case when these maxima are quite distinct and more or less proportional to each other.

Thus, in summary, for the $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) with chemical compression of the crystal lattice (Figure 2), we state:

(i) The data of X-ray $L_{III}$-absorption spectroscopy record changes in the effective valence of the europium ion from the stable state $Eu^{2+}$ ($x = 1$) to the state of homogeneous intermediate valence (IV) with $\vartheta_{eff} = 2.41 \pm 0.03$ (300 K) ($x = 0$) (see Section 3.2).

(ii) The transition is accompanied by a change in the temperature dependences of the resistivity and the thermopower; when observing from small values of the effective valence to higher values, then on the temperature dependence of the thermopower initially the "low" temperature maximum increases in absolute value (as a manifestation of the Kondo-like state (Kondo)), and later a "high" temperature maximum is observed (as a manifestation of homogeneous intermediate valence (IV)). It would be logical to use the generalizing term "state of interconfigurational fluctuations," since according to the data of $L_{III}$-absorption spectroscopy, the state of intermediate valence applies to both the compositions of the samples, which manifests mainly the "Kondo-like state," and the state of "intermediate valence," according to the above conditional division.

(iii) With the corresponding compositions of the samples, the coexistence of two maxima is observed, in particular in $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($x = 0$–$0.25$) (Figures 6 and 7).

If in this substitutional solid solution, together with the kinetic properties, we take into account the data on the effective valence of europium (X-ray $L_{III}$-absorption spectroscopy) and also take into account the available data of the effective valence of europium (obtained using the Mössbauer effect) and magnetic ordering obtained in work [8, 9], then it probably makes sense to conditionally divide the entire concentration range (sample composition) into three areas. Conditionally, since there may be coexistence in terms of properties within certain limits. It should rather be a division by dominant properties:

IV valence: 1-$EuCu_2Si_2$, 2-$Eu(Cu_{0.95}Ag_{0.05})_2Si_2$.

Kondo state: 3-$Eu(Cu_{0.875}Ag_{0.125})_2Si_2$, 4-$Eu(Cu_{0.75}Ag_{0.25})_2Si_2$, 5-$Eu(Cu_{0.50}Ag_{0.50})_2Si_2$.

Magnetic order: 6-$Eu(Cu_{0.25}Ag_{0.75})_2Si_2$, 7-$Eu(Cu_{0.125}Ag_{0.875})_2Si_2$, 8-$EuAg_2Si_2$.

Expecting a certain division, we tried from the very beginning to divide the entire range of concentrations in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) system into separate regions based on common properties. This was done throughout the text, highlighting these regions with a separate color starting from Figure 1, which was previously announced in the caption under Figure 1.

Characteristic parameters of the temperature dependences of thermopower and electrical resistance of the studied $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) samples are given in Table 1. For clarity (comparative analysis), the table is supplemented with the effective valence of europium samples of this solid substitution solution.

We observe two features in the temperature dependence of electrical resistance in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) system. The first feature is that the temperature dependences of $\rho$ ($EuAg_2Si_2$) and alloys closer in composition to $EuAg_2Si_2$ do not show signs of the influence of magnetic ordering. Most often, magnetic ordering is manifested by a drop in the value of resistivity below $T_N$. We may not have reached the magnetic ordering temperature for our samples. Temperature evolution of the Eu Mössbauer spectra for Eu $(Cu_{0.25}Ag_{0.75})_2Si_2$ shows [8, 9] that the magnetic transition occurs in the temperature range of 10–4.2 K and at 7 K, it is not yet finished. The second feature is that $\rho_{6\,K}$ ($EuAg_2Si_2$) > $\rho_{6\,K}$ ($EuCu_2Si_2$). This can be explained by the fact that in the case of $EuAg_2Si_2$, there is a component of scattering on the magnetic moments of Eu, which is absent in the case of $EuCu_2Si_2$ (even at 1.8 K [8, 9]).

In the temperature range (85–400 K), we conducted a study of the magnetic susceptibility of $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$). Insufficient temperature range does not allow us to provide guaranteed reliable magnetic parameters. But still, the effective magnetic $\mu_{eff}$ calculated according to the modified Curie–Weiss law $\chi = \chi(o) + C/(T-\theta p)$ per one formula unit in $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) varies from $7.7\,\mu_B$ in $EuAg_2Si_2$ to $5.0\,\mu_B$ in $EuCu_2Si_2$ and correlates well with the effective valence of the europium ion; the electronic component of magnetic susceptibility $\chi(o)$ increases from 4 to 44 cm$^3$/g, which is quite logical.

Temperature dependence of electrical resistance of samples in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ system indicates the metallic type of conductivity (Figure 7). Evidently, in addition to the phonon contribution $\rho_{ph}$ and the residual resistance $\rho_0$, there is an additional contribution, which is traditionally denoted as $\rho_{mag}$ ($T$):

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{mag}(T). \quad (1)$$

$\rho_{mag}$ ($T$) may, in particular, include scattering on the magnetic moments of atoms and the influence of the unstable valence state of europium. It is obvious that when analyzing the temperature dependence of kinetic properties, it is necessary to take into account both theoretical predictions (e.g., see Figure 5) and already obtained results on the change of effective valence with temperature [8, 9].

The difference between the temperature dependence of a compound with valence-unstable RE ions and the temperature dependence of an isostructural compound with stable RE ions allows us to reveal the influence of the valence-unstable europium ion on the nature of the temperature dependence of electrical resistance. In our case, it is legitimate to consider $EuAg_2Si_2$ and $LaCu_2Si_2$ as basic compounds with valence-stable europium ions, since their temperature dependences of electrical resistance, as already emphasized above, can best be described by the Bloch–Grüneisen law. The predominant scattering mechanisms in the case of $EuAg_2Si_2$ are phonon scattering and scattering by magnetic moments of Eu ions. In the case of $LaCu_2Si_2$ the phonon scattering dominates.

Since, for the reasons given above, we do not provide absolute values of resistivity, but provide normalized values, we will analyze $\rho_{mag}$ ($T$) of samples in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ system in the following way:

(a) $(\rho_{mag1}): \Delta\rho/\rho_{300} \approx \Delta_{Eu,Cu}(\rho/\rho_{300}) = \rho/\rho_{300}(Eu(Cu_{1-x}Ag_x)_2Si_2) - \rho/\rho_{300}(EuAg_2Si_2)$.

(b) $(\rho_{mag2}): \Delta\rho/\rho_{300} \approx \Delta_{Eu,Cu}(\rho/\rho_{300}) = \rho/\rho_{300}(Eu(Cu_{1-x}Ag_x)_2Si_2) - \rho/\rho_{300}(LaCu_2Si_2)$.

We caution that we consider only qualitative changes since we operate with reduced electrical resistance and not with absolute values. Nevertheless, the indicated approach is applied and makes it possible to determine the characteristic points or regions of the temperature dependence of $\rho_{mag1}$ or $\rho_{mag2}$ of the studied samples (Figure 8).

A comparison of the two figures for $\Delta_{Eu,Cu}(\rho/\rho_{300}) = f(T)$ and for $\Delta_{Eu,Ag}(\rho/\rho_{300}) = f(T)$ shows a qualitative similarity between them, and the ratio of copper–silver atoms in the sample determines the nature of the temperature dependence of the electrical resistance in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$). Because the specified ratio of copper and silver is directly related to the effective valence of europium, we conclude that the valence-unstable europium ion itself has a predominant effect on the temperature dependence of electrical resistance in $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$).

On the dependences, $\Delta_{Eu,Ag}(\rho/\rho_{300}) = f(T)$, we observe the presence of "low-temperature" and "high-temperature" maxima. The temperature of location of the high-temperature maximum on the temperature dependence of $\Delta_{Eu,Ag}(\rho/\rho_{300})$ is approximately the same for samples with $0.125 \leq x \leq 1.0$ and shifts sharply toward high temperatures for samples with $x = 0.0$ and $0.05$. In the investigated temperature range (6–400 K), the low-temperature maximum on the temperature dependence of $\Delta_{Eu,Ag}(\rho/\rho_{300})$ is clearly visible only for samples with $x = 0.125$ and $0.25$ (characteristic of concentrated Kondo systems (KKS)), and for other samples, we can note only the increase in resistance and the tendency to saturation. Such a course of the temperature dependence of electrical resistance is observed in the presence of the Kondo-type effect, when at a relatively high absolute value of the value $\Delta\rho_2 = \Delta_{Eu,Ag}(\rho/\rho_{300})$, with a decrease in temperature, there is an area of increase in the resistance of the sample. It can be assumed that changing the composition of the alloy in $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) creates conditions for scattering with spin reversal of $sd$-electrons on localized magnetic moments (Figures 7 and 8).

In a "sufficiently large" magnetic field, the low-temperature maximum of electrical resistance (at $T \sim 10$ K) of the Eu $(Cu_{0.875}Ag_{0.125})_2Si_2$ sample disappears (Figure 9).

This influence of the magnetic field extends to samples of other compositions, the temperature dependences of which show a low-temperature maximum. The reason for the suppression of the "Kondo-lattice state" may be a decrease in the exchange parameter $J_{sf}$, which determines the ratio between the efficiency of magnetic ordering by the RKKY mechanism and Kondo-type interactions. The interaction $J_{sf}$ between $4f$ and free electrons of the conduction band ($s$- and $d$-type)
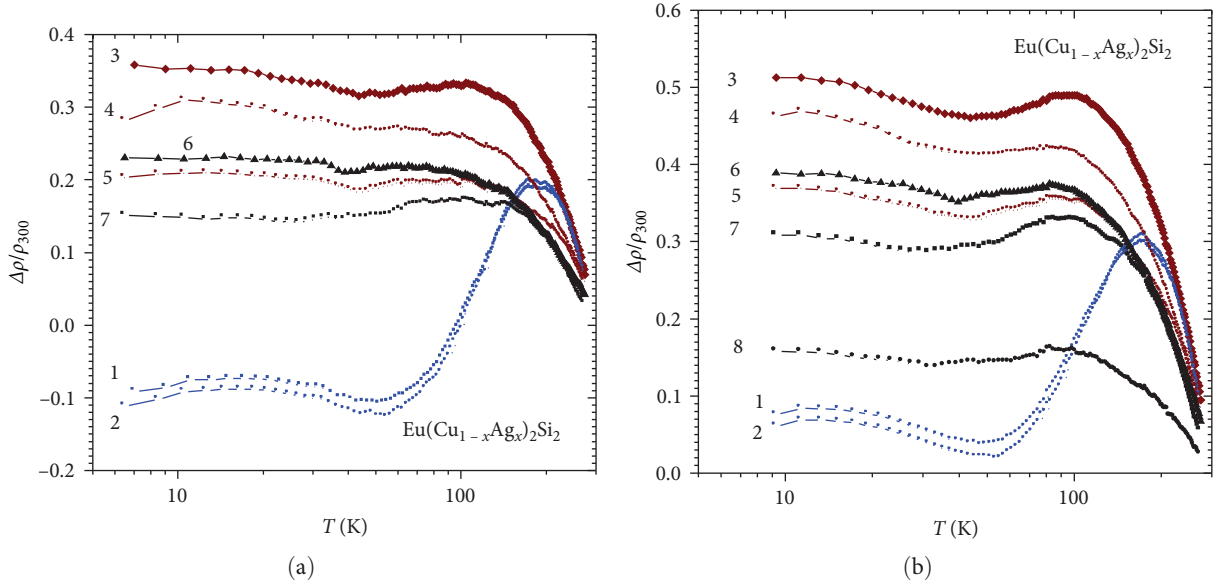
FIGURE 8: Temperature dependence of the selected part of the reduced resistivity $\rho_{mag}$ (T) in the system $Eu(Cu_{1-x}Ag_x)_2Si_2$ samples is defined as follows: (a) ($\rho_{mag1}$): $\Delta\rho/\rho_{300} \approx \Delta_{Eu,Cu}(\rho/\rho_{300}) = \rho/\rho_{300}(Eu(Cu_{1-x}Ag_x)_2Si_2) - \rho/\rho_{300}(EuAg_2Si_2)$, $x = 0.$ 0 (1); 0.05 (2); 0.125 (3); 0.25 (4); 0.50 (5); 0.75 (6); and 0.875 (7) and (b) ($\rho_{mag2}$): $\Delta\rho/\rho_{300} \approx \Delta_{Eu,Ag}(\rho/\rho_{300}) = \rho/\rho_{300}(Eu(Cu_{1-x}Ag_x)_2Si_2) - \rho/\rho_{300}(LaCu_2Si_2)$, $x = 0,$ 0 (1); 0.05 (2); 0.125 (3); 0.25 (4); 0.50 (5); 0.75 (6); 0.875 (7); and 1 (8).



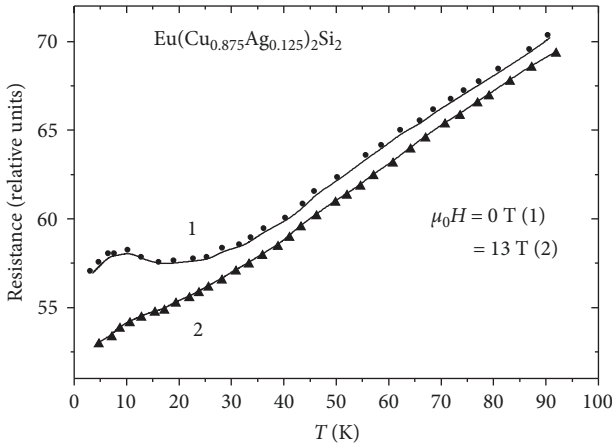FIGURE 9: Temperature dependence of resistance $Eu(Cu_{0.875}Ag_{0.125})_2Si_2$ in a magnetic field.

refers to the hybridization interaction $V_{sf}$ and depends on the energy proximity of the $f$-level ($E_f$) to the Fermi surface $E_F$: $J_{sf} \sim V_{sf}^2/(E_f - E_F)$ [4]. The state of the Kondo lattice is detected at small values of the excitation energy $\varepsilon_{ex}$ ($\varepsilon_{ex} \to 0$), that is, it can be assumed that $\varepsilon_{ex}$ increases in the magnetic field.

Summarizing, we can state that the analysis of the temperature dependence of the differential thermopower and electrical resistance, as well as the values of $\Delta_{Eu,Cu}$ ($\rho/\rho_{300}$) or $\Delta_{Eu,Ag}$ ($\rho/\rho_{300}$) in the studied substitutional solid solution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$), make it possible to predict the presence of the europium ion in a state of ICF (homogeneous intermediate valence) or Kondo-type state. And in combination with data from X-ray $L_{III}$-absorption spectroscopy, we can determine the root cause relationships between the composition of the

sample, the effective valence of the europium ion in the sample (the electronic state of the europium ion at a specific composition), and the nature of the temperature dependence of electrical resistance and differential thermopower.

In the substitutional solid solution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$), an increase in the concentration of silver brings the $4f$-configuration of europium closer to a divalent state with possible magnetic ordering that occurs at low temperatures in alloys with $x > 0.125$. Alloys with a small silver content when the temperature is lowered even to 1.8 K in the $^{151}Eu$ Mössbauer spectra contain only one peak, which clearly indicates the absence of magnetic ordering (Kondo shielding) [9]. It was assumed that for many europium compounds of the $EuM_2X_2$ type, which have developed spin fluctuations, the ground state at $\vartheta_{eff} < 2.33$ and isomeric shift $< -8.6$ can (but not necessarily) be magnetically ordered at the same time [16].

In [9], the beginning temperature of the establishment of magnetic order (9–10 K) in $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \leq x \leq 1$) was determined using Mössbauer spectroscopy. This temperature practically coincides with the temperature of the low-temperature maximum determined by us on the temperature dependence of thermopower (Figure 6). It can be assumed that the values of $T_K$ and $T_{RKKY}$ are close and that the effects of Kondo scattering and magnetic ordering compete.

From work [9], it is assumed that in the process of how the system moves to the time-averaged divalent state with increasing silver content, magnetically ordered domains appear at low temperatures. At $2x = 1.5$, the magnetic ordering extends to the entire volume of the sample at 4.2 K, while at $2x = 0.1$, it is almost absent even at 1.8 K. Thus, characteristic heterogeneity of pseudo-ternary solid solutions, can have a significant effect on the behavior on a microscopic scale of the studied systems. The number of silver ions replacing copper in close proximity

to europium determines whether the Eu of a given node has an intermediate valence or is divalent. In the latter case, Eu ions can participate in magnetic ordering. With increasing silver content, this component becomes dominant. Magnetic processes in $Eu(Cu_{1-x}Ag_x)_2Si_2$ phases develop due to growth and percolation between magnetically ordered micro volumes. According to the conclusions of the authors [9] from a microscopic point of view, the process of loss of magnetic order with increasing temperature occurs rather due to the gradual reduction of magnetic regions than through the destruction of spatial correlations of moments due to thermal excitation. Our studies of crystal formation processes and kinetic properties in the $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \le x \le 1$) system indirectly confirm the above statements or at least do not contradict.

By chance, we can acknowledge an incessant interest in the research of highly correlated systems of this type. In particular, we will single out the following works: multiple magnetic ordering in "heavy-fermion" $Ce_3Cu_4Sn_4$ [17]; superconductivity in "heavy-fermion" $CeCu_2Si_2$, antiferromagnetism, valence fluctuations, and heavy-fermion properties (antiferromagnetism, valence fluctuation, and heavy-fermion behavior in $EuCu_2 (Ge_{1-x}Si_x)_2)$ [3, 14, 18]. And to this day, we observe the continuation of intensive studies of systems (intermetallic compounds) based on Ce, Eu, and Yb with strong electron–electron correlations [19–22]. As noted in the introduction, many researchers use isostructural ternary compounds of the $RM_2X_2$ type that crystallize in the structural type $CeGa_2Al_2$ ($ThCr_2Si_2$). This indicates the effectiveness of their use for this kind of research. Absolute record holders among them are $EuCu_2(Si_xGe_{1-x})_2$ and $EuPd_2Si_2$. In the last period (2015–2022 years), one can list dozens of works on researching their properties (in particular, see [23, 24]) as well as review articles on compounds with strong electron–electron correlations (in particular, see [25, 26], valence fluctuation in Eu systems; strongly correlated $f$-electron Ce, Eu, Yb, U compounds with the $ThCr_2Si_2$ structure, respectively).

## 4. Conclusions

A substitutional solid solution $Eu(Cu_{1-x}Ag_x)_2Si_2$ exists within the range $0 \le x \le 1$. The peculiarity of its crystal formation is that when alloys are obtained in this system, a change in the silver–copper ratio leads to both monotonous spatial segregation (heterogeneity of the chemical composition of alloys that occurs during their crystallization) of elements in alloys and to the formation of certain "macro- and micro-heterogeneity" in composition within individual crystallites (while preserving the crystal structure of the alloy). Microheterogeneity in the immediate environment of the europium atom can form nonequivalent $4f$-electron configurations of europium, which impacts how the electronic structure is formed and, accordingly, on the physical properties of the alloys of the system. Substitution of silver for copper in solid solution alloys of substitution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \le x \le 1$) leads to lattice compression (chemical compression). Against the background of this lattice compression, the transition of the europium ion from the $Eu^{2+}$ state to the state with $\vartheta_{eff} = 2.41 \pm 0.03$ (300 K) occurs. The valence transition is monotonic and passes through the range of values $2.10 < \vartheta_{eff} < 2.16$, which is favorable for creating conditions for

the manifestation of the Kondo-type state and the region of coexistence of the Kondo state and the intermediate valence state of europium in $Eu(Cu_{1-x}Ag_x)_2Si_2$. The paper revealed a root-cause relationship between the valence state of europium and the electron transport properties in this substitutional solid solution. In general, the processes accompanying the replacement of silver with copper in the solid solution alloys of substitution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \le x \le 1$) can be attributed to critical phenomena, when microscopic fluctuations are correlated to macroscopic wavelengths, while fluctuations on all intermediate scales are also significant.

## Data Availability

All data supporting the study's concluded contained in the manuscript, and all data will be made available upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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