1. Introduction

Intermetallic cage compounds such as the type-I clathrates have been considered as promising compounds for the development of thermoelectric (TE) materials. Type-I clathrates have a cubic unit cell and an open crystal structure. The sp³ hybridized framework contains two types of cages, the smaller pentagonal dodecahedron and the larger tetrakaidecahedron (2 and 6 per unit cell, respectively) where guest atoms are situated [1]. Type-I clathrates have generally been considered to fulfill the criteria of the phonon glass-electron crystal (PGEc) concept in which the thermal conductivity exhibits low values similar to glasses and electronic properties are similar to good semiconductor/metal single crystals. However, recent work on clathrates has cast doubts on the general validity of the PGEc concept. For example, it was shown for the type-I clathrate Ba8Ni3.5Ge42.1 [2] that the Ba atoms cannot be considered as independent “rattlers”, isolated from the host cage, because the vibrational modes of the guest atoms hybridize with the framework-derived acoustic phonon modes over a wide region of the Brillouin zone. Based on these results, an alternative mechanism of low-pass filtering of acoustic phonon modes was introduced to explain the low lattice thermal conductivity in clathrates [3,4]. Low thermal conductivity materials are of interest for TE applications, and therefore the knowledge of the dominating scattering mechanism in these materials is essential.

The relatively small electrical resistivity $\rho$, large Seebeck coefficient $S$, and low thermal conductivity $k$ of type-I clathrates lead to relatively large dimensionless figure of merits $ZT = S^2 T \rho / k$ [5] in these materials, reaching for instance an experimental value of 1.35 at 900 K and with an extrapolated maximum of 1.63 at 1100 K for an n-type Ba$_8$Ga$_{16}$Ge$_{30}$ single crystal grown by the Czochralski technique [6]. Even the polycrystalline Ba$_8$Ga$_{16}$Ge$_{30}$ samples demonstrated comparable TE performance to single crystal at high temperatures via the optimization of the charge carrier concentration [7]. Also Si- or Ge-based systems reveal relatively high $ZT$ values, as it was shown for Ba$_8$Ga$_{16}$Si$_{46-x}$, where $ZT = 0.87$ was reached at 1000 K [8]. Therefore, Si- or Ge-based type-I clathrates are of interest for TE applications as well. Many attempts of substituting different transition metal elements for Si have been done in order to optimize the TE properties and enhance $ZT$ [9–11]. Au is interesting for its large atomic radius and mass, and its high electronegativity. Detailed investigations on Ba$_8$Au$_x$Si$_{46-x}$ revealed an n-type/p-type crossover near $x = 5.33$ as the Zintl concept predicts [12]. TE property measurements reveal relatively high $S$ and low $k$ values, but the electrical resistivity still remains a limiting factor for achieving $ZT$ higher than $\approx 0.2$ [11]. Si- or Ge-based type-I clathrates have also attracted attention due to the occurrence of...
superconductivity below 8 K in Ba$_8$Si$_{46}$ [13,14]. Among the rare-earthcontaining type-I clathrate systems, only for Eu a full occupation of all guest sites has been observed [15,16]. This is due to a large ionic radius of the divalent and earth alkalike-Eu in the 4$f^7$ ground state, which has stabilizing effect for substitution for Ba and Sr, for instance in Eu$_2$Ba$_6$Ga$_3$Si$_{36}$ and Eu$_{11}$Sr$_7$Al$_{10}$Si$_{36}$. Eu tends to occupy the smaller cage in the clathrate framework [17].

The preferential Eu occupancy of the smaller cages was confirmed by resonant X-ray scattering [18]. Eu-containing type-I clathrates are also of interest because Eu$^{2+}$ carries a large magnetic moment, and because the Seebeck coefficient is relatively high and the thermal conductivity is low.

An investigation of a series of the rare earth substituted Ba$_{0.04}$Eu$_{0.04}$Au$_{0.04}$Si$_{46}$–y clathrates revealed a rather high substitution level for Eu reaching about 1.5 per formula unit (f.u.) [19]. In this work we report on the low-temperature transport and magnetic properties of single-crystalline Ba$_{0.04}$Eu$_{0.04}$Au$_{0.04}$Si$_{46}$–y (x = 1.0, 1.68 and y = 4.77, 5.32) type-I clathrates. We focus on the substitution effects of Au for Si as electron acceptor and of Eu for Ba as heavier element with magnetic moment on the electrical and thermal transport. Additionally, detailed investigations of magnetic properties are discussed.

2. Experimental

2.1. Synthesis

Polycrystalline samples for crystal growth were synthesized by melting Ba (99.5%), Eu (99.5%), Au (99.95%), and Si (99.9999%) in a horizontal water cooled copper boat in argon atmosphere (6N) using high-frequency heating. The samples were homogenized by three remeltings. Single crystals of Ba$_{0.04}$Eu$_{0.04}$Au$_{0.04}$Si$_{46}$–y were grown using a floating zone technique with optical heating in a four mirror furnace (Crystal Corporation).

2.2. X-ray analysis

The crystal structure and phase purity of the samples were studied by X-ray powder diffraction (XPD) using a PANalytical X’Pert II diffractometer with Cu–K$_\alpha$$_2$ radiation at room temperature. The crystallographic parameters were obtained from Rietveld refinements using the Fullprof Suite software [20].

2.3. SEM/EDX

The phase compositions on polished samples were determined using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) in a Philips XL30 ESEM with an excitation of 30 keV. The standard deviation $\delta$ of the composition with a maximum of $\delta_{\text{max}} = 0.11$ at. % refers to spatial inhomogeneity of the sample and it does not contain systematic error of used method.

The error was estimated from a series of measurements at different positions of the sample.

2.4. Physical properties

The electrical resistivity $\rho$ and the Hall effect were measured using a Physical Property Measurement System (PPMS, Quantum Design, B = 9 T) in the temperature range 2 K $< T < 300$ K with a 6–point quasi AC technique in the PPMS using a horizontal rotator. For Hall effect measurements thin platelets samples were prepared in order to enhance the Hall voltage. The Hall resistivity $\rho_H$ was measured in magnetic fields up to 9 T. In order to eliminate the misalignment voltage, $\rho_H$ was measured at the angles 0° and 180° between the sample normal and the magnetic field. Heat capacity was measured on samples of $\approx$ 15 mg using a relaxation–type technique in a PPMS in the temperature range 1.8 K $< T < 300$ K. The samples were attached to the sample holder using thermal conduction paste Apiezon N, which was afterwards subtracted from the total signal.

The molar magnetic susceptibility $\chi (\chi = M/H)$ was measured using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 2 K $< T < 300$ K and in a field of $B = 0.1$ T. A field of $B = 2$ mT was applied during field cooling (FC) and zero field cooling (ZFC) experiments. The magnetization $M$ was measured in varying magnetic fields (0–7 T).

The Seebeck coefficient and thermal conductivity measurements were carried in a home-made device designed for a $^4$He flow cryostat, using a steady state heat flow method in the temperature range 4 K $< T < 300$ K. The temperature gradient along the sample is applied by a small resistance–chip heater with a room-temperature resistance of 10 kΩ. The heater is thermally decoupled from the sample holder through four manganin wires with a diameter of 25 μm and length of $\approx$ 10 cm. The temperature gradient along the sample was determined by a differential type–E thermocouple consisting of Chromel and Constantan. The thermal power $\rho$ was measured using a manganin wire with a diameter of 25 μm. The absolute temperature was measured by a Cernox thermometer in the entire investigated temperature range. A radiation shield was mounted around the sample in order to reduce the radiation effect.

3. Results and discussions

3.1. Phase analysis and structural properties

The single crystal grown by the floating zone technique is shown in Fig. 1. Single crystal Ba$_{0.04}$Eu$_{0.04}$Au$_{0.04}$Si$_{46}$–y was grown according to a technique developed in Ref. [21]. The nominal composition obtained from energy dispersive x-ray spectroscopy (EDX) data revealed a gradual change in the composition of Ba$_{0.04}$Eu$_{0.04}$Au$_{0.04}$Si$_{46}$–y along the crystal growth direction, while no sizable change in the composition was observed in the direction perpendicular to the crystal growth. The selected samples A and B, marked in Fig. 1, were used for physical and structural property measurements. EDX measurements revealed that both samples are homogeneous, impurity-free, and have the composition Ba$_{6.01}^{0.02}$Eu$_{1.01}^{0.04}$Au$_{4.04}^{0.02}$Si$_{41.01}^{0.02}$Si$_{41.01}^{0.02}$Si$_{41.01}^{0.02}$Si$_{41.01}^{0.02}$ for the sample A and sample B, respectively (see Table 1).

Rietveld refinements revealed that the X-ray powder diffraction (XPD) data of both samples, shown in Fig. 2, are well described by the space group $Pm$–3m (Table 1). Because Eu and Ba are hardly distinguishable due to their close X-ray atomic scattering factors the Eu content and the Eu site occupation were not distinguishable due to their close x-ray atomic scattering factors. The Eu content and the Eu site occupation were not distinguishable due to their close x-ray atomic scattering factors. The euclidean norm $x$ and the euclidean distance $d$ of a point $a$ were respectively (see Table 1).
The larger content of the smaller Eu in sample B should lead to a lattice shrinking which is, however, compensated by a higher content of larger Au [23]. The Eu substitution for Ba affects lattice parameter more efficiently compared to the Au substitution for Si due to the saturation effect for a high Au content (y > 5.2) observed in Ref. [12], therefore, a (sample A) > a (sample B).

### 3.2. Electronic properties

Overall, the electrical resistivities of Ba$_{8-y}$Eu$_y$Au$_3$Si$_{46-y}$ show metal-like characteristic ($\Delta\rho/\Delta T > 0$), with the room-temperature values of 1.62 and 1.23 $\text{m}\Omega\text{cm}$ for sample A and B, respectively (Fig. 3a). At low-temperatures, anomalies in $\rho(T)$, with their origin presumably in the ferromagnetic phase transition, are observed. The transition has been confirmed by heat capacity and magnetic susceptibility measurements (see later) - which revealed the Curie temperatures $T_C \approx 3$ K and 10 K for sample A and B, respectively (see Table 2).

Whereas the sample B clearly exhibits the electrical resistivity maximum at $T_C$ of 10 K (Fig. 3c), the sample A shows an upturn in $\rho(T)$ with decreasing temperature with no distinct maximum (Fig. 3b). This is most probably due to higher degree of structural disorder at the 6c site of the framework (smaller Au content) in sample A and due to presence of additional scattering mechanism. This could explain as well lower residual resistance ratio RRR of sample A compared to sample B (see Table 2). An enhanced negative magnetoresistance (MR) near the Curie temperatures (Fig. 3d) is a result of magnetic spin disorder scattering of s electrons by the localized Eu$^{2+}$ $4f$ electrons [16].
Fig. 4 shows the magnetic field-dependent Hall resistivities $\rho_H(\mu_0 H)$ at several temperatures. $\rho_H$ is linear in $\mu_0 H$ at temperatures above $T_C$, but deviates from linearity below $T_C$. Taking into account these observations, a one-band approach can be applied for the Hall coefficient $R_H$ evaluation above $T_C$. Fig. 5a shows that $R_H$ is negative for sample A, and positive for sample B, pointing to the dominance of electron-like and hole-like conduction, respectively. The $R_H$ values correspond to carrier concentrations of $2.38 \times 10^{27} \text{m}^{-3}$ and $2.21 \times 10^{26} \text{m}^{-3}$.

Fig. 3. (a) Temperature dependence of the electrical resistivities $\rho(T)$ of $\text{Ba}_{8-x}\text{Eu}_x\text{Au}_y\text{Si}_{46-y}$. The low-temperature close-up of $\rho$ showing the $T_C$ of sample A (b) and sample B (c). Temperature dependencies of the longitudinal magnetoresistance (MR) measured in applied magnetic field of 9 T.
The charge carrier concentration can be estimated from a simple framework are covalently bound to their four neighboring atoms, discussed as follows. If all hosts atoms forming a type consistent with the counting based on the Zintl concept which is agreement with the Hall effect measurements. They both are also nonlinear term in $r$ the sample's volume magnetization [24]. The linear behavior of $R_H(B) = \mu_H \cdot B$ vs. $\mu_0 M(B)/B$ (Fig. 5b and c) reveals the ratio $R/H$ of 1.6 and 23.7 for sample A and B, respectively. These values are typical for ferromagnetic semiconductors and metals, respectively [25]. The Hall mobilities $\mu_H$, evaluated from the $R_H$ above $T_C$ and the electrical resistivity data as $\mu_0 = R_H/p$, are shown in the inset of Fig. 5a. $\mu_H$, in absolute values, reaches 1.6 and 3.2 cm$^2$ V$^{-1}$ S$^{-1}$ at 300 K for sample A and B, respectively.

The temperature dependent Seebeck coefficients $S(T)$ are plotted in Fig. 6. The negative and positive sign of $S$ for $\text{Ba}_{8-\delta}\text{Eu}_{1.0}\text{Au}_{4.7}\text{Si}_{41.6}$ and $\text{Ba}_{8-\delta}\text{Eu}_{1.68}\text{Au}_{5.32}\text{Si}_{41.0}$, respectively are in agreement with the Hall effect measurements. They both are also consistent with the counting based on the Zintl concept which is discussed as follows. If all hosts atoms forming a type–1 clathrate framework are covalently bound to their four neighboring atoms, the charge carrier concentration can be estimated from a simple Zintl counting scheme $[\text{Ba}^{1+2+2+2+2+2+2+2}]_{8-\delta}[\text{Eu}^{1+2+2+2+2+2+2+2}]_{1.0}[\text{Si}^{4+6+6+6}]_{41.6+6.4}$. From this scheme, the difference in the charge carrier concentration $n$, and therefore in $S(T)$ cannot be due to different substitution levels $x$ of Eu but must be due to different Au concentrations $y$. This Zintl counting results in 0.95 electrons and 0.60 holes per formula unit for sample A and B, respectively, compared to 2.47 electrons and 0.45 holes per formula unit evaluated from the Hall coefficient measurements at 2 K. The Seebeck coefficient $S(T)$ is nearly linear in $T$. This behavior is expected for a diffusion Seebeck coefficient $S_D$ in the free–electron approximation [26] both at low temperatures, $S_D = n^2 k^2_0 m/|e| h^2 (3n^2)^{2/3} T$, and at high temperatures, $S_D = n^2 k^2_0 m/|e| h^2 (3n^2)^{2/3} T$, where $m$ is the effective mass of the

![Fig. 5.](image1) (a) Temperature dependence of the Hall coefficients $R_H(T)$ above $T_C$ of $\text{Ba}_{8-\delta}\text{Eu}_{1.0}\text{Au}_{4.7}\text{Si}_{41.6}$. The inset shows the temperature dependence of the Hall mobilities $\mu_H$, $R_H(B)$ plotted vs. $\mu_0 M(B)/B$ at 2 K of sample A (b) and sample B (c).

![Fig. 6.](image2) Temperature dependence of the Seebeck coefficients $S(T)$ of $\text{Ba}_{8-\delta}\text{Eu}_{1.0}\text{Au}_{4.7}\text{Si}_{41.6}$. Solid and dotted lines represent the low– and high–temperature limits of the free-electron diffusion Seebeck coefficient $S_D$, and dashed lines are the linear fits of experimental data.

### Table 3

Composition from EDX, lattice parameter $a$ from Rietveld refinement, type of major carriers, charge carrier concentration $n_{exp}$ evaluated experimentally at 2 K and 300 K and from the Zintl concept $n_{Zintl}$, and the effective mass $m$ at 300 K.

| Code  | Composition          | $a$  | $p/n$ | $|n|_{exp}$ (300 K) | $|n|_{exp}$ (2 K) | $|n|_{Zintl}$ | $m$ (300 K) |
|-------|----------------------|------|-------|-------------------|------------------|-------------|-------------|
| Sample A | $\text{Ba}_{8-\delta}\text{Eu}_{1.0}\text{Au}_{4.7}\text{Si}_{41.6}$ | 1.03898(4) | $n$ | 2.67 | 2.47 | 0.95 | 3.31 |
| Sample B | $\text{Ba}_{8-\delta}\text{Eu}_{1.68}\text{Au}_{5.32}\text{Si}_{41.0}$ | 1.03835(2) | $p$ | 1.80 | 0.45 | 0.60 | 3.87 |
charge carriers and \( n \) is the charge carrier concentrations evaluated from the \( R_H \). The experimental data of \( S(T) \) are of the same order as the diffusion Seebeck coefficient calculated from our \( R_H \) data and \( m = m_0 \) (see Fig. 6). We do not observe any anomaly in the linear behavior of \( S(T) \) near \( T_C \), which means that there are no sizable magnetic contributions to the Seebeck coefficient. Using the high—temperature free—electron approximation and room temperature values of \( n, m \) can be evaluated from the linear fit of \( S(T) \). This yields the effective mass \( m \) of 3.31 \( m_0 \) and 3.87 \( m_0 \) at 300 K for sample A and B, respectively. This result is consistent with previous observations of \( p \)-type carriers in type-I clathrates being heavier than \( n \)-type carriers [27].

### 3.3. Thermal properties

The temperature dependence of the heat capacitities \( C_p(T) \) of \( \text{Ba}_{8-x}\text{Eu}_x\text{Au}_{8}\text{Si}_{46-2y} \) is shown in Fig. 7. Up to 300 K \( C_p \) remains sizeably below the Dulong-Petit’s limit \( C_p = 3RN \), where \( R \) is the universal gas constant and \( N \) is the number of atoms per formula unit. Similar behavior was observed in several Si—based type—I clathrates [11-12]. At low temperatures, both samples show pronounced anomalies in \( C_p(T) \) (see inset of Fig. 7). These anomalies are associated with ferromagnetic phase transitions, as discussed above. The Curie temperature evaluated from \( C_p(T) \) is 3.1 K and 10.0 K for sample A and B, respectively. It is known that clathrates with \( n \)-type conductivity, low charge carrier concentrations, and centered guest atoms show a large maximum in \( C_p \) due to the freezing of three phonon Umklapp scattering processes at low—temperatures [3,28]. A large maximum in \( C_p \) in Ba6—Au6—Si46 is indeed observed for sample A (see Fig. 8). By introducing the transition metals, which act as efficient point scattering centers, \( C_p \) can be significantly reduced. Moreover, an increase of the guest free space in type-I clathrates also reduces \( C_p \) [29-31]. These behavior were found in \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{20}, \text{Ba}_8\text{Ni}_{16}\text{Ge}_{20}, \text{Ba}_8\text{Ga}_{16}\text{Si}_{20}, \text{Ba}_8\text{Au}_{16}\text{Si}_{46}, \) and \( \text{Ba}_8\text{Au}_{16}\text{Ge}_{20}, \text{Ga}_{16}, \text{Si}_{46} \) [12,31-34]. In order to determine the reason for crystalline—like behavior of the \( n \)-type sample A compared to glass—like behavior of the \( p \)-type sample B, \( C_p \) must be first of all extracted from the total \( k \) by subtracting the electronic contribution \( C_{el} \) using the Wiedemann—Franz relation. \( C_{el} = L_0T/j_0 \) with \( L_0 = 2.44 \times 10^{-8} \) V2 K−2. \( C_{el} \) is 13% and 21% of \( C_p \) at 150 K for sample A and B, respectively (inset of Fig. 8). Different \( C_p \) for sample A and sample B is due to different scattering mechanism of phonons and/or different effective mass of holes and electrons.

### 3.4. Magnetic properties

The temperature dependences of the inverse magnetic susceptibility \( \chi^{-1} = H/M \) of both samples measured in a magnetic field of 0.1 T are presented in Fig. 9. The low—temperature \( \chi^{-1} \) measured in a magnetic field of 2 mT (inset of Fig. 9) upon zero field cooling (ZFC) and field cooling (FC) show a different behavior below \( T_C \). While ZFC curve below \( = 3 \) K and 9 K for sample A and B, respectively, slightly saturates or decreases, both FC curves below these temperatures slightly rise. This behavior is typical for a ferromagnetic phase transition. The Curie temperatures \( T_C \) of 4.1 K and 11.1 K for sample A and B, respectively, were determined as anomaly in \( \chi^{-1} \) or \( \partial \chi^{-1}/\partial T \). Above \( T_C \), \( \chi^{-1}(T) \) data are well described by the Curie—Weiss law with Weiss
temperatures \( \theta \) of 6.0 K and 10.6 K for sample A and B, respectively, and an effective magnetic moment of 8.3 \( \mu_B \) per Eu ion for both samples. Small and positive Weiss temperatures suggest the existence of weak ferromagnetic interactions between the magnetic moments of Eu in both samples. The effective magnetic moments are close to the effective magnetic moment of 7.93 \( \mu_B \) for a free \( \text{Eu}^{2+} \) ion. The small deviations might be due to crystal electric field effects or due to a slightly lower amount of Eu in the samples (see below).

Fig. 10 shows the magnetization curves as a function of magnetic field at different temperatures between 2 K and 50 K. The largest change in magnetization is observed as the temperature crosses the ferromagnetic phase transition. The magnetization is almost saturated at 2 K and at 7 T and reaches values slightly higher than the saturation magnetization of 7 \( \mu_B \) of a free \( \text{Eu}^{2+} \) ion. This slight discrepancy can be due to fact that the actual Eu content in both samples is larger than the nominal composition obtained from EDX.

The inset of Fig. 10b is the closeup of \( M(H) \) at 2 K, showing weak hysteresis loops for both samples. The origin of ferromagnetism in \( \text{Ba}_8 \cdot \text{Eu} \cdot \text{Au} \cdot \text{Si}_{46-y} \) is the indirect exchange interaction between \( 4f \) moments via the charge carriers [24.35], known as indirect Ruderman–Kittel–Kasuya–Yoshida (RKKY) mechanism.

4. Discussions

In order to evaluate the lattice \( C_l(T) \), electronic \( C_b(T) \), and the magnetic \( C_{\text{mag}}(T) \) contributions to the total heat capacity, a nonmagnetic reference material would have to be subtracted as in Ref. [24]. Possible nonmagnetic reference materials from Ref. [12], with the compositions \( \text{Ba}_8 \cdot \text{Au}_{4.85} \cdot \text{Si}_{10.72} \) and \( \text{Ba}_8 \cdot \text{Au}_{5.59} \cdot \text{Si}_{8.01} \), are close to our compositions \( \text{Ba}_{6.63} \cdot \text{Eu}_{1.00} \cdot \text{Au}_{4.77} \cdot \text{Si}_{14.16} \) and \( \text{Ba}_{6.68} \cdot \text{Eu}_{1.03} \cdot \text{Au}_{3.32} \cdot \text{Si}_{41.0} \), respectively. Two Einstein temperatures were required to describe the anisotropic guest vibrations in two pentagonal dodecahedra and six tetrakaidecahedra cages, respectively. Sum of Debye \( N_D \) and Einstein oscillators \( N_E \) were adjusted according to their number of atoms per formula unit. The fit parameters are summarized in Table 4. Data are in agreement with previous studies on \( \text{Ba}_8 \cdot \text{Au} \cdot \text{Si}_{46-y} \) [12]; the Debye temperature \( \Theta_D \) and the lowest-lying Einstein temperature \( \Theta_{E1} \) decreases with increasing the Au content,
while $Q_{E2}$ increases.

Different scattering mechanisms have direct influence on the phonon relaxation time $\tau$ based on Matthiesen’s rule $\tau^{-1} = \sum \tau_i^{-1}$. In order to determine which kind of scattering mechanism is mainly responsible for a suppression of the maxima in $\kappa_{ph}$, Ikeda et al. proposed a modified Callaway model, in which the lowest-lying Einstein temperature $\Theta_{E1}$ and the average velocity of sound $v$, evaluated using the Debye temperature $\Theta_D$ and the lattice
parameter \( a \) as \( v = (\Theta_D \cdot k_b) / (b (6\pi^2 N / V)^{1/3}) \), where \( N \) is the number of atoms and \( V \) is the unit cell volume, are the main parameters for fitting the experimental data of \( \kappa_{ph} \) [41]. The model is valid well below \( \Theta_{E1} \); in our case we used \( T < (\Theta_{E1}/2) \). The average velocity of sound of 3332 m s\(^{-1}\) and 3231 m s\(^{-1}\) was evaluated for sample A and B, respectively, using \( \Theta_{D} \) of 360.9 K and 350.3 K evaluated from the high-temperature fit of \( C_{L}(T) \). The lowest-lying Einstein temperatures \( \Theta_{E1} \) of 82.3 K and 61.7 K for sample A and B, respectively, were used for the fitting procedure. Ikeda et al. proposed in his model, that by increasing of the defect scattering rate, the maximum of phonon thermal conductivity \( \kappa_{ph, max} \) is suppressed at \( T = \) const., while the suppression of \( \kappa_{ph, max} \) at \( T \neq \) const. is either by increasing of the phonon-electron scattering rate or the boundary scattering rate [41]. The experimental \( \kappa_{ph}(T) \) data of sample A were fitted using the modified Callaway model with \( \Theta_{E1} \) and \( v \) values considering phonon-electron scattering, phonon-boundary scattering, phonon-defect scattering, and Umklapp scattering processes (Fig. 13). Possible reason for the glass-like behavior of sample B are strong phonon-electron interactions, observed also in \( \text{Ba}_8\text{Ni}_{6-x}\text{Ge}_x \) [34]. Therefore, the prefactors of all scattering rates except for the phonon-electron scattering rate for sample B were fixed to the prefactors of sample A. From the fit parameters (see Table 5), we conclude that: (i) linear—temperature dependence of \( \kappa_{ph} \) \((T^3 \) power law in Fig. 13) indicates that Umklapp scattering is the dominant process at low temperatures. (ii) The phonon mean—free path \( l = v \cdot \tau \), where \( \tau \) is the phonon relaxation time and \( v \) is the average velocity of sound, is, with \( \approx 120 \mu m \) for both samples, indeed smaller than the size of the crystal. Therefore, phonon-boundary scattering is negligible in both samples. (iii) The prefactor of the phonon-electron scattering term is significantly enhanced for sample B, showing that this process is dominant and responsible for the glass—like \( \kappa_{ph} \) of \( p \)-type sample B.

Suekuni et al. published for type-I clathrates an universal dependence of the phonon thermal conductivity \( \kappa_{ph} \) at a constant temperature on the guest free space \( R_{free} \) (Fig. 14), defined as \( R_{free} = R_{cage} - (R_{G-ion} + R_{\text{cov}}) \) \([29,41]\), where \( R_{cage} \) is the distance between the 6d and 24k site, \( R_{G-ion} \) is the radius of the guest ion, and \( R_{\text{cov}} \) is the average value of the host atoms \([41,42]\). The covalent ionic radius of 1.61 Å, 1.35 Å, 1.37 Å, and 1.11 Å were used from Refs. [23,29]. While the transition metal (TM) free type-I clathrates clearly show \( \kappa_{ph} (R_{free}) \) dependence indicated by the solid line, TM containing type-I clathrates revealed also \( \kappa_{ph} (R_{free}) \) trend, but different from TM free materials (see Fig. 14). \( \text{Ba}_8\text{Eu}_{x}\text{Au}_{y}\text{Si}_{46-y} \) samples lay within the error bar on the line of TM containing type-I clathrates. Reason why TM free— and TM containing type-I clathrates show different \( \kappa_{ph} (R_{free}) \) dependencies is due to fact that the bonding between TM of the framework and the guest atoms of Ba has additionally to the ionic character as well the covalent character compared to TM free type-I clathrates. This has been shown for example in \( \text{BaAs}_{13,33}\text{Ge}_{43} \) system [43].

The Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions are responsible for the ferromagnetic (FM) ordering of \( \text{Ba}_8\text{Eu}_{x}\text{Au}_{y}\text{Si}_{46-y} \) samples. It was shown for \( x \) - and \( \beta \) - \( \text{Eu}_x\text{Ga}_{16}\text{Ge}_{30} \) that the shortest Eu–Eu distances lies within the first oscillation of the RKKY function [24], and thus can explain the FM behavior in both, \( \alpha \) - and \( \beta \) - \( \text{Eu}_x\text{Ga}_{16}\text{Ge}_{30} \). Additionally, calculating the \( F(R) \) function within the RKKY formalism, where \( J_{RKKY} = \sum_j^{|xy|} \beta_j (2k_{Fj} R_{ij} \cos(2k_{Fj} R_{ij}) - \sin(2k_{Fj} R_{ij})) / R_{ij}^4 \) and \( k_{F} = (3\pi^2 n)^{1/3} \) and \( F(R) = (2k_{Fj} R_{ij} \cos(2k_{Fj} R_{ij}) - \sin(2k_{Fj} R_{ij})) / R_{ij}^4 \), the higher \( T_C \) for \( \beta \)-compared to \( \alpha \) - \( \text{Eu}_x\text{Ga}_{16}\text{Ge}_{30} \) was in agreement with higher absolute values of \( F(R) \) [24]. Fig. 15 shows \( F(R) \) functions for \( \text{Ba}_8\text{Eu}_{x}\text{Au}_{y}\text{Si}_{46-y} \) samples, calculated using the charge carrier concentrations at their \( T_C \). Longer period of oscillation for sample B is due to smaller charge carrier concentration compared to sample A. Assuming the partial occupancy of Eu atoms at the 2a site, the nearest-neighbor (NN) Eu\(^{2+} \)(2a) - Eu\(^{2+} \)(2a) distance in both samples is \( \approx 9.0 \) Å. Using the sign convention of \( F(R) < 0 \), \( S_i \cdot S_j > 0 \) and \( F(R) > 0 \), \( S_i \cdot S_j < 0 \) for the ferromagnetic and antiferromagnetic (AFM)-type of order, respectively, \( F(R) \) function at their

Table 5

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Fig. 15. $F(R) = |(2k R_1 cos(2k R_1) - \sin(2k R_1))|/R_1^2$ of Ba$_6$Eu$_{0.9}$Au$_{3.0}$Ge$_{3.8}$, at their respective $T_c$ as a function of the distance $R$ from a given magnetic moment with spin S. Black and red solid circles represent the $F(R)$ functions for both samples at the nearest-neighbor (NN) and at the next-nearest-neighbor (NNN) Eu$^{2+}$ (2a) - Eu$^{2+}$ (2a) distances, respectively. The inset shows the temperature dependence of the heat capacity ($C_p(T)/C_0$) of sample B measured in applied magnetic field of 0 T and 9 T. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Eu$^{2+}$ (2a) - Eu$^{2+}$ (2a) distances for both samples is, in absolute values, relatively small, compared to Eu$_6$Ga$_{16}$Ge$_{30}$ [24]. Furthermore, according to Fig. 15, sample A should exhibits an AFM-type of order, opposite to magnetic susceptibility measurements, which clearly demonstrate FM-type of order in both samples. Small and positive Weiss temperature of 6.0 K and 10.6 K for sample A and B, respectively, shows relatively small strength of FM-type of interactions, which can compete with an AFM-type of order. This could explain relatively small magnitude and different polarity of $F(R)$ function at their NN distances in our samples. The 2a lattice is exactly half-filled by Eu atoms in sample A. Therefore, the next-nearest-neighbor (NN) Eu$^{2+}$ (2a) - Eu$^{2+}$ (2a) interaction at $\approx 10.39$ Å are more probable compared to the nearest-nearest (NNN) at $\approx 9.0$ Å, and thus the $F(R)$ function of sample A falls into negative FM regime (see Fig. 15). The scenario of preferable NNN interactions in sample A is supported by the fact that substituted Eu atoms, which create a local lattice distortion, avoid any clustering. Thus, probability of NNN interaction is enhanced. Large fraction of Eu atoms (84% occupancy) at the 2a site in sample B tends to prefer the NN interaction with an FM-type of order compared to a small fraction of an AFM-type of NNN interaction.

Phan et al. showed that Eu$_6$Si$_3$Ge$_{40}$Ge$_{20}$ undergoes not only FM transition at $T_c \approx$ 35 K [39], but also a secondary magnetic transition at $T_L \approx$ 10 K [39], indicated as a result of the magnetic interaction between the Eu$^{2+}$ at the 2a and the 6d site. The secondary magnetic transition in Eu$_6$Ga$_{16}$Ge$_{30}$ was observed e.g. as a broad shoulder in the magnetic heat capacity [24] and in the magnetic entropy change [39].

Heat capacity data plotted as $C_p/T$ vs. $T$ for sample B clearly exhibits an anomaly at $T_c \approx$ 3.7 K (see inset of Fig. 15) compared to sample A with no observed anomaly (for clarity of Fig. 15 not shown). By applying external magnetic field of 9 T the secondary magnetic transition shifts towards higher temperatures (see inset of Fig. 15), which is a clear indication of no Kondo interactions in Ba$_6$Eu$_{0.9}$Au$_{3.0}$Si$_{3.8}$ system, where application of pressure up to 18 kbar enhances the magnetic ordering temperature [17]. The origin of secondary magnetic transition at 3.7 K in sample A might be due to a small fraction of NN interaction, which gives an AFM-type of order.

5. Conclusions

Single-crystalline Ba$_6$Eu$_{0.9}$Au$_{4.77}$Si$_{3.9}$Ge$_{3.6}$ and Ba$_6$Eu$_{0.9}$Au$_{4.68}$Si$_{3.3}$Ge$_{3.5}$ samples were grown by a floating zone technique and investigated by measurements of the electrical resistivity, the Seebeck coefficient, the Hall coefficient, the heat capacity, the thermal conductivity, and the magnetic susceptibility. In agreement with the Zintl concept, $n$-type and $p$-type behavior for Ba$_6$Au$_{4.7}$Si$_{3.6}$Ge$_{3.7}$ and Ba$_6$Au$_{4.6}$Si$_{3.2}$Ge$_{3.5}$ respectively, was confirmed by Seebeck and Hall coefficient measurements. Both samples are metal–like and ferromagnetic with relatively low Curie temperatures. The RKKY interaction model was used in order to explain the FM-type of order in which the NNN and the NN interactions play a major role in sample A and B, respectively. The thermal conductivity of Ba$_6$Eu$_{0.9}$Au$_{4.77}$Si$_{3.9}$Ge$_{3.6}$ and Ba$_6$Eu$_{0.9}$Au$_{4.68}$Si$_{3.3}$Ge$_{3.5}$ shows a large maximum at low temperatures, which is drastically suppressed for Ba$_6$Eu$_{0.9}$Au$_{4.7}$Si$_{3.6}$Ge$_{3.7}$ and Ba$_6$Eu$_{0.9}$Au$_{4.6}$Si$_{3.2}$Ge$_{3.5}$ respectively. From the modified Callaway model, proposed by Ikeda et al. [41], we concluded that Umklapp scattering process is dominant at low temperatures for both samples and enhanced phonon–electron scattering in Ba$_6$Eu$_{0.9}$Au$_{4.77}$Si$_{3.9}$Ge$_{3.6}$ and Ba$_6$Eu$_{0.9}$Au$_{4.68}$Si$_{3.3}$Ge$_{3.5}$.

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