Synthesis of a Cu-Filled Rh₁₇S₁₅ Framework: Microwave Polyol Process Versus High-Temperature Route

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Supporting Information

ABSTRACT: Metal-rich, mixed copper-rhodium sulfide $Cu_{3-\delta}Rh_{34}S_{30}$ that represents a new Cu-filled variant of the $Rh_{17}S_{15}$ structure has been synthesized and structurally characterized. Copper content in the [CuRh₈] cubic cluster was found to vary notably dependent on the chosen synthetic route. Full site occupancy was achieved only in nanoscaled $Cu_3Rh_{34}S_{30}$ obtained by a rapid, microwave-assisted reaction of CuCl, $Rh_2(CH_3CO_2)_4$ and thiosemicarbazide at 300 °C in just 30 min; whereas merely Cu-deficient $Cu_{3-\delta}Rh_{34}S_{30}$ (2.0 $\geq \delta \geq 0.9$) compositions were realized via conventional high-temperature ceramic synthesis from the elements at 950 °C. Although $Cu_{3-\delta}Rh_{34}S_{30}$ is metallic just like $Rh_{17}S_{15}$, the slightly enhanced metal content has a dramatic effect on the electronic properties. Whereas the $Rh_{17}S_{15}$



host undergoes a superconducting transition at 5.4 K, no signs of the latter were found for the Cu-derivatives at least down to 1.8 K. This finding is corroborated by the strongly reduced density of states at the Fermi level of the ternary sulfide and the disruption of long-range Rh–Rh interactions in favor of Cu–Rh interactions as revealed by quantum-chemical calculations.

1. INTRODUCTION

Metal-rich chalcogenides of transition metals lie in focus of a vast research playground thanks to their various electronic properties stemming from metal-metal interactions, including complex magnetic ordering patterns, superconductivity, charge density waves, etc. However, nanoscaling of these materials generally represents a considerable synthetic challenge. Among downscaling techniques, microwave-assisted polyol synthesis is steadily gaining popularity thanks to such benefits as rapidness, high product yield, and a higher degree of product crystallinity as compared to syntheses in other solvents.^{1–5} Nanosized noble-metal chalcogenides are envisioned for many applications, for instance, as catalysts with high activity,^{6–9} and they may also demonstrate physical properties differing from those of the bulk analogues due to confinement effects.¹⁰

Bulk $Rh_{17}S_{15}$ exhibits a rare case of superconductivity arising from the presence of strongly correlated 4d electrons of rhodium at the Fermi level and demonstrates a critical field (H_{c2}) value well above the Pauli paramagnetic limit.^{11–13} Ever since superconductivity in $Rh_{17}S_{15}$ was discovered, a number of attempts to study the influence of chemical composition on the critical parameters have been repeatedly undertaken.^{14,15} It was shown that partial substitution of rhodium atoms by iron, nickel or palladium¹⁴ hinders superconductivity at least down to 1.5 K, whereas iridium doping (up to ca. 6 atom %) considerably decreases the critical temperature down to ca. 3.5 K.¹⁵ Although the previous works assumed that substitution only takes place within the rhodium sublattice, the $Rh_{17}S_{15}$ framework offers enough room for additional guest atoms, for example, in the rhodium-enclosed cubic voids that may host relatively small cations. Coinage metals may be promising candidates, especially in view of the reported significant amounts of copper in the naturally grown samples of *miassite* mineral $(Rh_{17}S_{15})$.¹⁶ On top of that, minor solubility of copper in the rhodium sulfide in the temperature range between 540 and 900 °C has also been accounted for ref 17. To the best of our knowledge, effects of copper doping on the physical properties of $Rh_{17}S_{15}$ have not been investigated yet.

The present work is filling in this gap, as it provides a comprehensive characterization of the crystal structure and physical properties of nanoscaled and bulk $Cu_{3-\delta}Rh_{34}S_{30}$ phases that were synthesized by a microwave-assisted approach and the conventional high-temperature route, respectively. The samples were studied by means of powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). Magnetic susceptibility and transport measurements down to 1.8 K

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revealed metallic behavior and quenching of the superconducting transition.

One of the highlights of $\rm Cu_{3-\delta}Rh_{34}S_{30}$ is a filled-up cubic void in the $\rm Rh_{17}S_{15}$ framework and the consequent formation of the extremely rare, intermetallic $[\rm CuRh_8]$ cluster^{18,19} that has not been observed in covalently bonded systems so far, let alone transition-metal chalcogenides. Chemical bonding between the incorporated Cu atoms and the Rh–S framework in Cu_3Rh_{34}S_{30} was characterized by delocalization indices^{20,21} and domain-averaged Fermi-hole analysis.^{22,23}

Another remarkable feature is the varying occupancy of the copper site that appears to correlate with the chosen synthetic route. Complete filling could only be achieved via a lowtemperature, microwave-assisted polyol process, which, moreover, provided Cu₃Rh₃₄S₃₀ in the shape of nanoparticles with the average diameter of 13 nm. Earlier this advanced technique has been successfully adapted to abundant elemental-metal nanoparticles, $^{4,24-27}$ binary alloys, $^{28-31}$ and oxygen-containing materials, $^{32-35}$ but there have been only a handful of reports on preparation of oxygen-free ternary compounds.³⁶⁻⁴⁰ Metal-rich Pd₃Bi₂S₂ and Pd₃Bi₂Se₂ nanoparticles are among the few recent, successful applications of the method.¹⁰ The first instance of nanosized Cu₃Rh₃₄S₃₀ reported herewith can be also juxtaposed with the earlier attempts to produce sulfides in the form of nanoparticles in the Cu-Rh-S system by another wet chemistry approach. The latter did not result in any ternary compounds but yielded core-shell Cu1.94S@Rh2S3 nanoparticles with the Cu_{1.94}S nanoprisms covered by Rh₂S₃ instead.41

2. EXPERIMENTAL SECTION

2.1. Microwave-Assisted Synthesis. Ethylene glycol (Fluka, 99%) was dried under vacuum at 100 °C for 4 h prior to use. The starting materials CuCl (Alfa Aesar, 99.9%), $Rh_2(CH_3CO_2)_4$ (Alfa Aesar, 98%+), and thiosemicarbazide (Sigma-Aldrich, 99%+) were obtained from commercial sources and were used without purification. Microwave synthesis was performed in a dynamic mode in a CEM Discover System operating at 300 W and 2.45 GHz. Solution (15 mL) containing precursors was placed in a 35 mL Pyrex tube with a silicon cap and heated to 300 °C in 3 min and held at this temperature for 30 min. After the termination of the reaction, the tube was rapidly cooled using a high-pressurized air flow. The obtained black precipitate was washed several times with ethanol to remove the residual solvent. Finally, the product was dried under vacuum at room temperature overnight. The sample obtained by the microwave-assisted synthesis will be referred to further in the text as Sample 1.

2.2. High-Temperature Synthesis. $Cu_{3-\delta}Rh_{34}S_{30}$ samples were prepared from the elements following the conventional solid-state route. Fine powders of Cu (ABCR, 99.9%), Rh (Merck, 99.9%), and S (Alfa Aesar, 99.99%) taken in the stoichiometric ratio of the target compound were placed into a silica ampule. The evacuated ampule was cooled with liquid nitrogen during sealing to prevent evaporation of sulfur. The sealed ampule was heated in a muffle furnace to 950 °C with 10 °C/h heating rate and held at this temperature for 7 d. After that, the sample was removed from the furnace and allowed to cool to room temperature. Samples obtained by high-temperature synthesis are labeled as Samples 2–6.

2.3. Powder X-ray Diffraction. PXRD measurements of the samples were performed on a PANalytical X'Pert Pro diffractometer (Cu K α 1 radiation; $\lambda = 1.540$ 56 Å; germanium monochromator), a flat-plate silicon sample holder was used. LaB₆ was used as an internal standard. Temperature-dependent synchrotron powder diffraction data ($\lambda = 0.400$ 01 Å) were collected at the ID22 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble. The structure refinement was performed with the JANA2006 software.⁴²

2.4. Electron Microscopy. The SEM images were collected on a Hitachi SU8020 microscope. An acceleration voltage of 2 kV and a current of 10 μ A were used to generate the SEM images in the secondary electron scanning mode. The energy-dispersive X-ray spectra (EDX) were collected using an Oxford Silicon Drift X-Max^N detector at an acceleration voltage of 30 kV and with 100 s of accumulation time. For the determination of the composition, ~10 points per sample were measured. Transmission electron microscopy (TEM) investigations were performed in an FEI Tecnai-T20 microscope operated at 200 kV. For a specimen preparation Cu₃Rh₃₄S₃₀ nanoparticles were dispersed in ethanol with an ultrasonic bath and then deposited on a holey carbon grid.

2.5. Resistivity and Magnetization Measurements. The resistivity measurements were performed using a 14 T Quantum Design PPMS equipped with a variable-temperature insert for cooling to 1.8 K. The resistance was measured using the standard four-probe technique. Magnetization was measured using an MPMS rf-SQUID-magnetometer. For both resistivity and magnetization measurements the powder was pressed to a pellet for 1 min with the applied pressure of 0.1 GPa.

2.6. Electronic Structure Calculations. Band structure calculations were performed for Cu₃Rh₃₄S₃₀, with the respective lattice parameters and atomic positions obtained from the powder X-ray refinement. Scalar relativistic all-electron full-potential local orbital calculations employing LDA PW92 functional⁴³ were performed by using the FPLO-9 code.44 The Blöchl-corrected linear tetrahedron method⁴⁵ with a $12 \times 12 \times 12$ *k*-mesh was employed after checking for convergence with respect to the number of k-points. Scalar-relativistic projector augmented wave (PAW) calculations⁴⁶ were performed with the ABINIT code^{47,48} utilizing the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.49 Modified ABINIT PAW data sets⁵⁰ have been used with plane-wave energy cutoff of 18 hartree and a $2 \times 2 \times 2$ k-point grid. Subsequent analysis of chemical bonding was performed within the framework of the quantum theory of atoms in molecules (QTAIM).⁵¹ Electron sharing indices^{20,21} and domain-average Fermi-hole (DAFH) anal-ysis^{22,52} were evaluated employing domain overlap matrices computed from PAW calculation results according to ref 53.

For comparison, the electronic structure of the parent compound $Rh_{17}S_{15}$ was also calculated within the same scheme as described above for $Cu_3Rh_{34}S_{30}$ but using the reported structural data.⁵⁴ Although $Rh_{17}S_{15}$ is believed to be a correlated superconductor,^{11–13} the LDA density of states for this compound was found to reproduce the shape of the photoemission spectrum and to give an accurate estimate of the Sommerfeld coefficient.⁵⁵

3. RESULTS AND DISCUSSION

3.1. Synthesis. The route used for the synthesis of Cu₃Rh₃₄S₃₀ employs a polyol reduction of the Rh³⁺ and Cu⁺ precursors under microwave irradiation in the presence of thiosemicarbazide as a sulfur source. It is worth noting that the exact reaction pathway is still unknown; however, possible key factors for the formation of Cu₃Rh₃₄S₃₀ can be identified. The polyol process favors a consecutive reduction of Rh³⁺ and Cu⁺ to metallic intermediates, while the reduction rate is to a large extend determined by the redox potential of the corresponding redox couples. The growth and nucleation of the metallic particles are accompanied by a reaction with sulfur ions released by the thiosemicarbazide feedstock. Because of stability of complexes formed by thiosemicarbazide and both rhodium and copper cations^{56–59} the polyol-mediated conversation occurs at relatively high temperature (300 °C) that leads to formation of relatively small particles. In the kinetically driven, nonequilibrium process, copper might in fact be rendered in a rhodium-sulfur framework enabling the environment for the Cu₃Rh₃₄S₃₀ ternary phase formation. It is interesting to note that the microwave synthesis in the binary Rh-S system does



Figure 1. Morphology of the $Cu_3Rh_{34}S_{30}$ sample obtained by microwave synthesis. SEM, low-resolution and high-resolution (HRTEM) images of the nanoparticles (upper). The dimensioning in the HRTEM image corresponds to ~1 nm. EDX mapping (lower) shows the presence of uniformly distributed Cu, Rh, and S.

Table 1. Crystallographic and EDX Data ^{**} for the $Cu_{3-\delta}Rh_{34}S_{30}$ Compou
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3:34:30 3:34:30 2(2) 0.94(2) 0.96(1) 1.94(1) 8(8) 0.90(1) 0.9(1)
2(2) 0.94(2) 0.96(1) 1.94(1) 8(8) 0.90(1) 0.9(1)
8(8) 0.90(1) 0.9(1)
544(1) 9.9660(1) 9.9664(1) 9.9407(1)
6.40(1) 989.79(1) 989.95(1) 982.33(3)
9 7.70 7.70 7.66
6.73 6.55 6.55
2, 2.32 3.10, 3.47 4.48, 5.04 4.48, 5.04
5, 3.33 3.17, 3.48 4.56, 5.05 4.56, 5.05
9 1.49 1.13 1.13
9 5 2, 5, 9

"Space group Pm3m (221), Z = 1, 2θ range from 7 to 130°, Cu K α 1 radiation. U_{iso} for all the Rh atoms as well as U_{iso} for all the S atoms are constrained. $U_{iso}(Cu1) = U_{iso}(Rh^*)$ constrained.

not lead to the formation of pure $Rh_{17}S_{15}$ but to an amorphous phase consisting of particles with varying Rh/S ratio as determined by EDX. Several consecutive annealing steps at 500 °C are required for the formation of crystalline $Rh_{17}S_{15}$. In contrast, $Cu_3Rh_{34}S_{30}$ exhibits a high degree of crystallinity even in the form of as-prepared nanoparticles.

3.2. Morphology. Figure 1 shows a typical morphology of the as-prepared $Cu_3Rh_{34}S_{30}$ nanoparticles (Sample 1, see Table 1). Particle-size calculations employing the Scherrer equation⁶⁰ yield an average particle size of 13.5 ± 1.1 nm. TEM study showed that the nanoparticles tend to form spongelike networks that impede shape and size estimation. Individual nanoparticles have irregular shapes and often can be a subject to twinning and intergrowth, whereas their diameters hardly reach 10–20 nm. The high-resolution imaging of individual particles further revealed that the nanoparticles demonstrate a good crystallinity. The lattice spacing is ~1 nm, which is perfectly in line with the crystal structure of $Cu_3Rh_{34}S_{30}$ determined below.

3.3. Crystal Structure Determination. Initial indexing of the PXRD pattern collected with laboratory X-ray source for Sample 1, prepared by the microwave-assisted synthesis (see Table 1), suggested a primitive cubic unit cell with the lattice parameter a = 9.9891(2) Å. The powder pattern resembled that of Rh₁₇S₁₅ generated from the reported structural data,⁵⁴

whereas the calculated lattice parameter was ~1% larger than that of $\text{Rh}_{17}\text{S}_{15}$ (a = 9.9093(2) Å⁵⁴). We started the refinement by taking the atomic coordinates of $\text{Rh}_{17}\text{S}_{15}$ as a model. The refinement reached convergence with $R_p = 7.63$ and $R_B = 10.57$, but the residual electron density was high, indicating that the model was not complete. Visualization revealed that the highest positive maximum in the difference-Fourier map is located in the position (0, 1/2, 1/2), in the center of a cube built by the Rh1 atoms (Figure 2). No significant positive maxima were found close to the Rh or S sites.

From the X-ray data only, it was not possible to conclude which chemical species occupies the mentioned void. Therefore, additional experiments were undertaken to explore the quasi-binary sections $Rh_{17}S_{15}$ -Rh, $Rh_{17}S_{15}$ -S, and $Rh_{17}S_{15}$ -Cu via a high-temperature route. It was revealed that Rh or S excess leads to formation of impurities, namely, metallic Rh and $Rh_{3}S_{4}$, respectively, confirming that $Rh_{17}S_{15}$ -Cu mixtures yielded cubic phases with a varying lattice parameter dependent on the Cu content (Samples 2–5). It is worthwhile to note that minor solubility of Cu in $Rh_{17}S_{15}$ was reported,¹⁷ but the Cu site preference in this structure was not determined. The crystal structure refinement of these cubic $Cu_{3-\delta}Rh_{34}S_{30}$ phases employing the crystal structure of $Rh_{17}S_{15}$ as the initial model produced a high residual electron density peak in the center of



Figure 2. Section $0 \le x, y \le 1$ in z = 0 of the difference Fourier map after the initial Rietveld refinement for Sample 3. The maximum corresponds to the position of the Cu atom, which is not included in the structural model. The Rh1 atoms are shifted out of the cutoff plane by 1.45 Å, whereas the Rh2, Rh3, and S2 atoms lie in it.

the $[Rh1]_8$ cubes, similarly to the case of Sample 1. This position was refined as partially occupied by Cu. In the case of Sample 1, prepared by microwave-assisted route, the 3c Wyckoff site lying in (0, 1/2, 1/2) was found to be fully occupied. The Cu content derived from the structure analysis is in good agreement with the EDX results. The crystallographic data and refinement parameters are summarized in Table 1. The atomic coordinates, the atomic displacement parameters, as well as the list of selected interatomic distances are given in the Supporting Information (Tables S1 and S2). Typical XRD patterns for the freshly produced nanoparticles as well as for the Cu_{3- δ}Rh₃₄S₃₀ samples, obtained by high-temperature synthesis, are given in Figures S1 and S2.

It is interesting to note that the presence of an unaccounted electron density maximum with (0, 1/2, 1/2) fractional coordinates was reported in the crystallographic report on the Ni_{9.54}Pd_{7.46}S₁₅ compound with mixed Ni/Pd sites.⁶² Our findings allow us to suggest that Ni atoms may also occupy the cubic void in the structure similarly to Cu in Cu_{3- δ}Rh₃₄S₃₀.

Thus, $Cu_{3-\delta}Rh_{34}S_{30}$ has the filled $Rh_{17}S_{15}$ crystal structure. The complex framework can be visualized as consisting of four types of polyhedra (Figure 3). Empty $[S2_{12}Rh2_{6/2}]$ cages (cluster A) represent cuboctahedra built of S2 atoms with Rh2



Figure 3. Crystal structure of $Cu_{3-\delta}Rh_{34}S_{30}$ in the polyhedron representation. Rh and S atoms are shown in green and orange, respectively. Cu atoms occupy the centers of the blue cubes.

atoms located slightly above each of the square faces. The latter atoms link the type A clusters with Rh3-centered $[Rh3S1_4Rh2_{2/2}]$ octahedra (cluster B) via common corners, so that the cuboctahedral and octahedral clusters form a ReO3type arrangement. The cubic void in this arrangement is occupied by a [Rh4S3₆] octahedron (cluster C). The resulting octahedral interstitials framed by four B clusters and two C clusters accommodate isolated Cu-centered [Cu1Rh1s] cubes (cluster D). The distance between the Cu1 and Rh1 atoms is found to be 2.556(1) Å in Cu₃Rh₃₄S₃₀. Similar [CuRh₈] units occur also in the CuRh₂Sn Heusler compound¹⁸ as well as in the Al_{0.82}Cu_{0.11}Rh alloy¹⁹ with the CsCl structure. However, the distance between the Cu and Rh atoms in Cu₃Rh₃₄S₃₀ is significantly shorter than in the intermetallic compounds listed above (2.661(1) Å and 2.573(1) Å for CuRh₂Sn and Al_{0.82}Cu_{0.11}Rh, correspondingly).

PXRD analysis was performed to monitor changes in the crystal structure caused by the Cu incorporation. Apparently, there is a correlation between the lattice parameter and the Cu content in the $Cu_{3-\partial}Rh_{34}S_{30}$ samples, namely, the lattice parameter increases with the increasing amount of copper (Figure 4). However, it is important to note that only samples



Figure 4. Dependence of the lattice parameter (at room temperature) from the Cu content (derived from PXRD data) in the series of $Cu_{3-\delta}Rh_{34}S_{30}$ samples. Sample 1 was obtained by a microwave-assisted polyol process at 300 °C, Samples 2 to 4 were obtained by high-temperature synthesis, and Samples 5 and 6 were obtained in the same batch at 1100 °C. The Cu content of Sample 6 was estimated by fitting the lattice parameter values (given in Table 1).

with $\delta \geq 0.9$ were accessible by high-temperature synthesis. Copper excess in the starting composition results in emergence of the Cu_{2-x}S (PDF No. 29–578) impurity (synthesis temperature 950 °C, Sample 3). At the synthesis temperature close to the melting point (~1100 °C), two Cu_{3- δ}Rh₃₄S₃₀ phases with different Cu occupancies can be obtained in the same batch, accompanied by Rh (PDF No. 5–685) and Rh₃S₄ (ICSD No. 410813) impurities. One of the Cu_{3- δ}Rh₃₄S₃₀ phases corresponds to the maximal observed Cu concentration ($\delta \approx 0.9$, Sample 5), and its lattice parameter a = 9.9665(1) Å resembles that for Sample 4; the second one with a = 9.9414(1)Å (Sample 6) corresponds to $\delta \approx 2.0$ (see Figure 4). Thus, we can conclude that the maximal Cu occupancy achievable by high-temperature synthesis at 950 °C is close to 70% ($\delta \approx 0.9$).

The microwave-promoted chemistry is able to overcome this limitation. The $Cu_3Rh_{34}S_{30}$ sample (Sample 1), prepared in the polyol process, has a significantly larger cell parameter than

Samples 2–6. The dependence of the lattice parameter on the Cu content follows Vegard's law.

Thermal stability of Cu₃Rh₃₄S₃₀ was studied to understand how postannealing may affect the copper content. The asprepared powder of Sample 1 was sealed in a quartz ampule and annealed at 300, 500 and 950 °C for 7 d. The annealing at 300 and 500 °C does not introduce changes in the crystal structure and leads to a crystallinity improvement only. However, at 950 °C Cu₃Rh₃₄S₃₀ decomposes with a formation of the Cu_{3- δ}Rh₃₄S₃₀ composition with $\delta \approx 1.7$ and the Cu_{2-x}S (PDF No. 29–578) binary phase. The sintering also induces a significant grain growth and results in formation of ~100–500 nm wide microcrystallites with a micrometer-sized polyhedral shape. This shape resembles the morphology of another sample obtained by high-temperature synthesis (Figure 5). EDX



Figure 5. SEM images of $Cu_{3-\delta}Rh_{34}S_{30}$ microcrystallites obtained after annealing of Sample 1 at 950 °C for 7 d (top left). Morphology of a $Cu_{3-\delta}Rh_{34}S_{30}$ sample obtained by high-temperature synthesis (Sample 3, top right). EDX mapping of a single microcrystallite found in Sample 1 after annealing confirms the compositional inhomogeneity induced by the sintering (lower).

mapping on a separately lying crystallite confirms the presence of phases with different copper content, which is in line with our XRD measurements. The heating of Sample 1 to 1100 °C in an alumina crucible under the argon flow resulted in a complete decomposition with formation of metallic Rh (PDF No. 5–685) and ~5 atom % $Cu_{2-x}S$.

3.4. Physical Properties Characterization. The electrical resistance was measured on a pressed pellet made from Sample 1, prepared by the microwave-assisted synthesis. When the sample cooled from room temperature, the resistance decreased by ~20%, passing through a minimum at 15 K and increasing slightly with decreasing temperature to 1.8 K (Figure 6). Between 40 and 225 K the measured resistance shows a thermal hysteresis. Below 40 K resistance measured during cooling agrees with that for increasing temperatures. Moreover, it was confirmed that this effect is reproducible over several heating-cooling cycles and that it is independent of applied magnetic fields up to 14 T (see Figure S3). In contrast to $Rh_{17}S_{15}$,^{11–13} no signature of a superconducting transition was observed within the investigated temperature range down to 1.8 K. The dynamic susceptibility, measured at 16 Hz, also shows no sign for a superconducting transition down to 0.35 K (not shown).

The static magnetic susceptibility M/H in the temperature range between 1.8 and 300 K is shown in Figure 7. The



Figure 6. Resistance vs temperature of a pellet made from $Cu_3Rh_{34}S_{30}$ powder (Sample 1). No superconducting transition down to 1.8 K was observed.



Figure 7. Static magnetic susceptibility vs temperature at various applied fields for the $Cu_3Rh_{34}S_{30}$ powder (Sample 1). (inset) A peak in M/H appearing only in the upsweep.

magnetization measurements as well show no superconducting transition in line with the resistivity data. However, an anomaly appears in the range between 40 and 55 K, exclusively for increasing temperatures. We presume that this maximum of the static susceptibility and the branch in the resistivity could be a hint for a phase transition of $Cu_3Rh_{34}S_{30}$ at 45 K, leading to a hysteresis. Our synchrotron powder diffraction data for Sample 4, which demonstrates a magnetic behavior similar to Sample 1 (not shown), do not reveal any presence of structural phase transition down to 30 K. However, a hysteretic behavior of the lattice parameter was observed in the temperature range corresponding to the hysteretic loop in the resistivity measurements (see Figure S4).

The field dependence of the magnetization is shown in Figure 8. Whereas for T > 100 K, an almost temperatureindependent diamagnetic behavior was found, for T < 100 K, additional spin-paramagnetic contribution leads to an increase of the susceptibility. From the slope of the magnetization in Figure 8a, a diamagnetic susceptibility of $-0.211(1) \ \mu \text{emu}/$



Figure 8. Magnetization vs external magnetic field on a pellet made from $Cu_3Rh_{34}S_{30}$ powder (Sample 1) at (a) T = 50 K and (b) T = 2.0 K.



Figure 9. Calculated electronic total and partial DOS for $Rh_{17}S_{15}$ (a, b) and $Cu_3Rh_{34}S_{30}$ (c, d).

 $(Oe \cdot g)$ at 50 K was calculated, somewhat less than the susceptibility of typical insulators, such as silica glass. This is a consequence of Pauli-paramagnetic contributions of the conduction electrons.

After subtracting the diamagnetic contribution of the field sweep at 2.0 K, it became possible to fit the remaining spinparamagnetic contribution using the Brillouin function, as it is expected for non-interacting, diluted paramagnetic impurities (Figure 8b). The values for gJ and J were used as fitting parameters, leading to J = 3/2 and gJ = 2.24. From the extracted saturation magnetization M_s , the amount of paramagnetic impurities was calculated to be only ~0.05 atom %. It is important to note that, according to Abrikosov and Gorkov,⁶³ 0.2–1.2 atom % of magnetic impurities are typically needed for

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suppressing the superconductivity through magnetic impurities. Thus, the suppression of superconductivity in $Cu_3Rh_{34}S_{30}$ is most probably caused by changes in the electronic structure as compared with $Rh_{17}S_{15}$ (see below).

3.5. Electronic Structure Calculations and Chemical Bonding Analysis. The total density of states at the Fermi level for $Rh_{17}S_{15}$ was found to be 104 states eV^{-1} unit cell⁻¹, which is larger than the previously reported calculated value,⁶⁴ but fits to the estimation based on the heat capacity data.⁵⁵ For Cu₃Rh₃₄S₃₀, N(E_F) gets reduced to 38 states eV^{-1} unit cell⁻¹. For both compounds, the largest contribution to the total density of states (DOS) at the Fermi level stems from the Rh(4d) states (Figure 9).

Among four independent Rh positions, Rh1, building the cubic voids, has the strongest effect on N($E_{\rm F}$), with its 4d states accounting for ~60% of the total DOS in the case of the pure Rh₁₇S₁₅ and 50% for Cu₃Rh₃₄S₃₀. Rh1(4d) states are hybridized with S(3p) states at $E_{\rm F}$. In the pure Rh₁₇S₁₅, the fractions of the S2(3p) and S3(3p) states are essentially equal at the Fermi level, whereas the contribution of S1(3p) is 25% smaller. The contribution of the Cu(3d) states in Cu₃Rh₃₄S₃₀ amounts to only ~2% of the total DOS, whereas Cu(4s) states are not present at $E_{\rm F}$. The considerable reduction of N($E_{\rm F}$) in Cu₃Rh₃₄S₃₀ cannot be explained by a simple rigid band model.

Calculated QTAIM basin populations, characterizing the effective atomic charges,⁵¹ revealed an electron transfer of 0.23 electrons from Cu atom to the Rh–S framework (see Table S4). Thus, the S3 QTAIM charge becomes more negative, whereas Rh1 charge gets more positive. Since this electron transfer is rather small, the bonding between Cu and the host framework should have an essential degree of covalence, which can be characterized using electron delocalization indices (DI), denoted as δ_{A-B} , which show a degree of electron pair exchange between QTAIM atoms A and B,²⁰ and directly related to covalent bond orders.²¹

The DI value between Cu and Rh1 given in Table S4 is close to those between Rh1 atoms but higher than the DI value between Cu atoms in face-centered cubic (fcc) Cu (δ_{Cu-Cu} = 0.26)⁶⁵ indicating essential sharing and strong interaction. The DI between Cu and the closest S3 atom ($\delta_{Cu-S} = 0.15$) indicates a certain degree of direct covalent interaction between them. DI values between nearest rhodium atoms and between Rh1 and S3 atoms in Cu₃Rh₃₄S₃₀ tend to decrease in comparison with $Rh_{17}S_{15}$ (by at most 0.1, Table S4). Together with the increased difference between the QTAIM charges of Rh1 and S3 atoms, this points toward slightly enhanced ionicity of the Rh-S bonding in Cu₃Rh₃₄S₃₀ in comparison to Rh₁₇S₁₅, and to the redistribution of the electron sharing in favor of the interaction with Cu. To visually characterize the bonding situation of the Cu atom and to reveal the changes of bonding situation of Rh1 upon the incorporation of copper, DAFH orbitals^{22,52} were evaluated for these atoms. DAFH orbitals deliver visual quantitative representation on how a QTAIM atom utilizes its electrons for bonding. Representation of bonding with DAFH orbitals has been shown to be able to recover many useful chemical concepts.⁶⁶

Besides the orbitals, corresponding to the core electrons, which are not relevant for describing the chemical bonding situation for Cu, there are five orbitals with d-like shape, one with s- and three with p-like shapes (Figure 10). Their shape, occupation numbers, and degree of localization (given in Table S5) resemble those for the copper DAFH orbitals in metallic fcc Cu (Figure 10 in ref 23) and were found to be typical for



Figure 10. DAFH orbitals in $Cu_3Rh_{34}S_{30}$ centered at the Cu atom. (a) One of the d-like orbitals with occupation 1.91; (b) s-like orbital with occupation 0.62; (c) one of p-like orbitals with occupation 0.20. Orbital isosurfaces are drawn for the amplitude 0.02. Orbital phases are colored in accordance to the attached color scale.

bonding in simple metals, such as fcc Cu or bcc Na.²³ Thus, the DAFH orbitals for copper in $Cu_3Rh_{34}S_{30}$ are akin to those for metallic Cu despite the presence of two S atoms at the distance of 2.66 Å. The most remarkable difference is the smaller occupation numbers and the reduced localization inside the reference basin of the orbitals in comparison to the fcc Cu,²³ which is in line with the electron transfer from Cu to the Rh–S framework mentioned above.

Among nine DAFH orbitals corresponding to the valence electrons of the Rh1 atom forming $[Rh1_8]$ cubes in $Rh_{17}S_{15}$ and $Cu_3Rh_{34}S_{30}$, five have the shape resembling d-orbitals. Their occupation numbers are in the range between 1.0 and 1.7, and 55-90% of their orbital charge is inside the Rh1 QTAIM basin for both compounds. They are similar to d-type DAFH orbitals of the fcc Cu mentioned above,²³ but they are more involved in the bonding with the neighbor atoms, as it can be seen from the their lower localization degree (see Table S5). Another four DAFH orbitals have a shape similar to the p-type orbitals of fcc Cu^{23} and also represent the multicenter bonding with the nearest atoms. Their occupation numbers are between 0.2 and 0.3, and 10-20% of their orbital charge is inside the Rh1 QTAIM basin for $Rh_{17}S_{15}$ and $Cu_3Rh_{34}S_{30}$ as well.

Among these orbitals there is none that can be undoubtedly attributed to the direct metal—metal bonding (as, for instance, orbitals reported in Figure 1d in ref 67 or in Figure 3 in ref 53). In the case of Rh₁₇S₁₅, the shape of the d-orbitals points toward the presence of direct Rh—Rh interaction (Figure 11a), which contributes to the δ_{Rh-Rh} value to almost one-half. In contrast, a similar DAFH orbital in Cu₃Rh₃₄S₃₀ (Figure 11c) is reoriented toward the Cu atom, so that its contribution to δ_{Rh-Rh} drops to ~0.25 of its value in Rh₁₇S₁₅. At the same time this orbital contributes nearly one-third of δ_{Cu-Rh} .

To sum up, one may conclude that upon the introduction of Cu into the structure, the interactions between Rh and S become more ionic, whereas direct Rh–Rh bonding is weakened in favor of bonding between Cu and Rh, which looks similar to the bonding in fcc Cu.²³ Doping studies suggested that the interatomic distance between the corners of the Rh cube needs to be short enough for realization of superconducting properties; thus, the rhodium substitution by iridium led to an elongation of the metal–metal contacts in the cubes, which results in a gradual decrease of T_c with increasing doping level.¹⁵ In this respect, the filling of the cubic void with Cu can be regarded as another possibility of weakening the Rh–Rh bonding by redirection of the electron sharing in favor of Cu–Rh interactions, which seems to result in the quenching of superconductivity.



Figure 11. DAFH orbitals for one of the Rh1 atoms forming $[Rh1_8]$ cube in $Rh_{17}S_{15}$ and $Cu_3Rh_{34}S_{30}$. (a, c) d-type orbitals with occupation numbers 1.47 (a) and 1.43 (c); (b, d) p-type orbitals with occupation numbers 0.20 (b) and 0.22 (d). Orbital isosurfaces are drawn for the amplitude 0.04. Orbital phases are colored in accordance to the attached color scale.

4. CONCLUSIONS

The series of the $Cu_{3-\delta}Rh_{34}S_{30}$ (2.0 $\geq \delta \geq 0.9$) with a Cu-filled Rh₁₇S₁₅ structure has been synthesized for the first time. The conventional high-temperature route yielded samples with $\delta \geq$ 0.9 only, whereas the microwave-assisted polyol synthesis is able to overcome this limitation and results in nanostructured stoichiometric Cu₃Rh₃₄S₃₀. The copper intercalation in Rh₁₇S₁₅ suppresses the superconductivity, since the Rh-Rh interactions, which contribute decisively to the superconductivity in the binary sulfide, are weaker. The bonding situation of the copper atoms, occupying the cubic interstices built of Rh atoms, is shown to be similar to that in metallic Cu and other simple metals. We expect that the new facile approach proposed in this article will result in further exploration of microwave-assisted methods, resulting in easier preparation methods for nanosized noble metal chalcogenides. A $Cu_{3-\delta}Rh_{34}S_{30}$ (2.0 $\geq \delta \geq 0.9$) compositional series with a new Cu-filled Rh₁₇S₁₅ structure has been synthesized and comprehensively characterized for the first time. Unlike earlier reports on transition-metal substitution for rhodium in Rh₁₇S₁₅, copper appears to fill voids in the host framework, thus building rare [CuRh₈] cubic arrangements. Copper intercalation in Rh₁₇S₁₅ suppresses superconductivity along with weakening of the Rh-Rh interactions that contribute decisively to the superconductivity in the parent binary sulfide. The bonding situation of the copper atoms in the [CuRh₈] entities is shown to be similar to that in copper metal and other simple metals. The gained insight into interrelations

between the crystal structure of a doped phase, its physical properties, and the underlying bonding scenario contributes to a solid fundament of better understanding, on which future attempts of chemical modifications to tailor the physical properties can be based.

Whereas the conventional high-temperature route yielded $Cu_{3-\delta}Rh_{34}S_{30}$ samples with $\delta \geq 0.9$ only, the microwaveassisted polyol synthesis was able to overcome this limitation and resulted in nanostructured stoichiometric $Cu_3Rh_{34}S_{30}$. We expect that the described new, facile approach will promote further exploration of microwave-assisted methods and ultimately result in easier preparation methods for nanosized noble-metal chalcogenides.

Carbon-supported rhodium sulfides, that is, $Rh_{17}S_{15}$, demonstrate high electrocatalytic activity for hydrogen evolution and oxidation^{7,8} and show prospects for industrial recovery of high-value chlorine gas.⁹ Hence studies of catalytic properties of the Cu-filled derivatives are encouraged, as they may open new vistas.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01102.

Typical XRD patterns, atomic coordinates, atomic displacement parameters tables, temperature evolution

of the lattice parameter, details of electronic structure calculations, and chemical bonding analysis (PDF)

Accession Codes

CCDC 1546894 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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