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High-Pressure Synthesis, Structure, and Electrical Property of Iodine-Filled Skutterudite $I_{0.9}Rh_4Sb_{12}$—First Anion-Filled Skutterudite

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An iodine containing skutterudite compound $I_{0.9}Rh_4Sb_{12}$ was prepared by the reaction of the element mixture with an iodine excess composition (I:Rh:Sb = 1.5:4:12) at 5−12 GPa and 850 °C. Rietveld structural analysis revealed that this is the first anion-filled skutterudite crystallizing in the space group *Im-3* with a lattice constant of $a = 9.29997(6)$ Å. X-ray photoelectron spectroscopy proved the oxidation state of iodine to be I^-. The compound is semimetallic with a resistivity of 9.9 mΩcm at 300 K. Band structure and density of states calculations suggested that the bands near the Fermi level are mainly composed of Rh-p, Rh-d, and Sb-p orbitals; the contribution of iodine is not large.

Introduction

High-pressure and high-temperature synthesis often provides new compounds having interesting structures and remarkable physical properties. In particular, by applying this synthetic approach to the elements of Groups 13, 14, and 15, which have a tendency to form covalent bonds, some interesting frameworks are obtained. These frameworks include fullerene-like cages, single or double square mesh nets, and tunnel structures in and between which some guest species can be accommodated.

Clathrate and skutterudite compounds are typical examples of such compounds. Many compounds having such structures are prepared under ambient pressure, but some interesting compounds have also been obtained by high-pressure synthesis. For example, superconducting barium silicon clathrate compounds $Ba_{24}Si_{100}$ and $Ba_{8-x}Si_{46}$ were prepared by reaction at 1.5 and 3 GPa, respectively.[1,2] $Ba_{8-x}Si_{46}$ has the so-called type I clathrate structure composed of face-sharing Si_{24} tetrakaidecahedra and almost regular Si_{20} dodecahedra, with barium ions situated at the center. The framework is composed of only four-bonded sp^3 silicon atoms. This compound is the first superconductor having an sp^3 silicon 3D network and shows a critical temperature (Tc) of 5−9 K, depending on the composition determined by x.[3] $Ba_{24}Si_{100}$ has another type of clathrate structure (type III) with Tc = 1.4 K.[4]

More than one hundred Group 14 clathrate compounds with different compositions have been reported. In most clathrate compounds, the guest ions are alkali or alkaline earth ions. The iodine-doped type I clathrate compound $I_8[Ge_{44}I_2]$ is an example where the I^- ions are placed in the Ge cages as anionic guest species.[5] The silicon analogue $I_8[Si_{44}I_2]$ is obtained by high-pressure and high-temperature reactions (5 GPa and 700 °C).[6] Recently, many more clathrate compounds containing iodine have been reported.[7]

Like the clathrate structures, the skutterudite structure contains large cages and can accommodate guest ions. The structure with guest ions present is called filled skutterudite (Figure 1). The host atoms are mostly pnictogens (Pn) and Group 8 and 9 transition metals (M), and guests are mainly rare earth (Ln) and alkaline earth (A) elements. The guest ions are situated at the center of icosahedral Pn_{12} cages.

Filled skutterudite compounds have been studied intensively because they exhibit properties characteristic of f-electrons: heavy fermion behavior, curious superconductivity, and non-Fermi liquid behavior. A variety of combinations of Pn, M, and Ln elements have been tested.[8−14]

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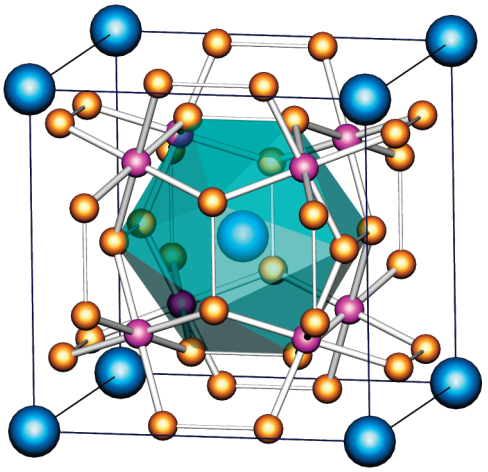

Figure 1. Crystal structure of filled skutterudite compounds. The blue circles represent guest atoms, which are mainly rare earth and alkaline earth elements. The yellow and red circles represent pnictogens (P, As, and Sb) and Groups 8 and 9 transition metals, respectively.

Comprehensive studies by Shirotani et al. revealed that a high-pressure condition is necessary for preparing some filled skutterudite compounds of heavy rare earth elements.[15−18] More recently, new compounds containing Group 14 elements in the host cage have been reported, including a new superconductor $BaPt_4Ge_{12}$.[19−26] However, skutterudite compounds containing anionic species in the cages have not yet been reported. In this study, we have prepared a new member of the skutterudite family of compounds containing iodine in the guest site using a high-pressure and high-temperature reaction.

Experimental Section

Powders of Rh (Nilaco 99.9%), Sb (Katayama chemical 99.999%), and I_2 (Sigma-Aldrich 99%) with an atomic ratio of I:Rh:Sb = 1.5:4:12 were mixed well in an agate mortar. The mixture was placed into an h-BN container with 2.5 mm inner diameter and 5 mm depth, and reacted in a Kawai-type high-pressure system. The detailed assembly of the reaction cell is described elsewhere.[27] The mixture was allowed to react at 12 GPa and 850 °C for 1 h, and then it was quenched to room temperature. After cooling, the pressure was gradually decreased to ambient pressure.

The composition of the product was determined by electron probe microanalysis (EPMA). First, we confirmed our sample specimens contained only I, Rh, and Sb by qualitative analysis. For quantitative analysis, Rh metal (Nilaco 99.9%) and Sb (Katayama Chemical 99.999%) were used as standards. Because of a lack of an appropriate standard for iodine, the atomic ratio of iodine was calculated from the residual after the determination of the Rh and Sb contents.

The data for the structural analysis were collected by means of a conventional X-ray diffractometer (Bruker AXS D8) by Cu Kα radiation using the step scan mode (0.00741°/step) from 18° to 120°. A nonreflecting Si plate was used as a sample holder to reduce the background. The structural refinement was performed using the RIETAN-2000 multipurpose pattern-fitting program.[28]

X-ray photoelectron spectroscopic (XPS) measurements were performed using a Shimazu ESCA 3400. Magnetic susceptibility measurements were performed using a SQUID magnetometer, applying a magnetic field of 5000 Oe. Electrical resistivity was measured on a rectangular specimen with dimensions of 1.80 × 1.00 × 0.50 mm^3, which was prepared by polishing the bulk product with sandpaper. We measured the resistivity of this specimen by a four-probe method using DC from room temperature to 2 K.

Band structure calculation was performed using the WIEN2k package with a general potential LAPW code.[29] Some parameters used were as follows: RMT, 2.5 for I and Rh and 2.32 for Sb; Gmax, 12; R-MT × k-max, 7.

Results and Discussion

Synthesis and Chemical Analysis. Because iodine is a highly volatile element, 50% excess amounts of iodine were used in the preparation to compensate for loss during the sample packing in h-BN cells and in the high-pressure and high-temperature reactions. After the reaction at 12 GPa and 850 °C, polycrystalline samples with a silver metallic luster were obtained. The compound was stable under ambient conditions. The X-ray powder diffraction study revealed that all peaks could be indexed as a cubic cell with a = 9.29997(6) Å; the peak pattern was very similar to that of other skutterudite compounds.[30] The lattice parameter was larger than that of $RhSb_3$ (9.2322 Å),[30] suggesting that iodine was successfully introduced into the structure of $RhSb_3$.

To confirm the presence of iodine, chemical analysis of the sample was performed by EPMA, and an averaged composition of $I_{0.95}Rh_{3.91}Sb_{12}$ was determined. The specimens were mostly a single phase of the iodine rhodium antimonide with very small amounts of RhSb, Rh_2Sb, and $RhSb_2$. Although most parts of the specimens showed compositions close to the stoichiometric composition of $I_xRh_4Sb_{12}$ with x = 1, a few domains had smaller amounts of iodine with $0.72 < x < 0.9$, suggesting some nonstoichiometry around the iodine site.

We performed a similar reaction at 5 GPa and 850 °C, and obtained almost the same compound with the lattice

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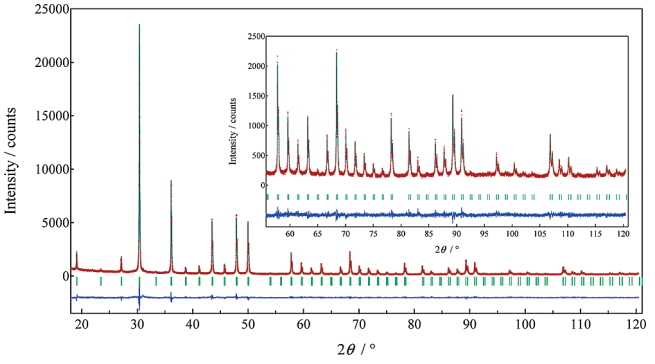

Figure 2. Result of Rietveld analysis of the iodine-filled skutterudite compound $I_{0.9}Rh_4Sb_{12}$. The observed data are shown as small red crosses, the calculated fits and difference curves as solid lines. Tick marks indicate calculated peak positions.

constant $a = 9.2937(1)$ Å, slightly smaller than that of the 12 GPa sample. A similar compound with the lattice constant $a = 9.2906(6)$ Å was also obtained from a mixture of nonfilled skutterudite $RhSb_3$ and I at 12 GPa and 850 °C. Furthermore, from the reaction of $RhSb_3$ and I at 12 GPa and 300 °C, a similar skutterudite compound with $a = 9.301(1)$ Å was obtained, though the crystallinity was relatively low because of the low reaction temperature. In contrast, we tried reactions of $RhSb_3$ and I in evacuated silica tubes, but $RhSb_3$ did not react with iodine up to 600 °C.

We also examined whether the iodine is extracted from the iodine-doped skutterudite. Heated in an evacuated silica tube at 500 °C for 12 h, the iodine-doped skutterudite partially changed to $RhSb_3$. Considering that $RhSb_3$ did not react with I in evacuated silica tubes up to 600 °C, a high-pressure condition was necessary for the synthesis of this iodine-doped compound. High-pressure synthesis has the advantage that iodine can be retained in the reaction system up to high temperatures.

Structure Analysis. The iodine-doped skutterudite was obtained at rather low temperature (300 °C) at 12 GPa from a mixture of $RhSb_3$ and I. It changed to $RhSb_3$ at 500 °C in an evacuated silica tube. These observations strongly indicate that iodine is introduced as the guest species in the large cages of the $RhSb_3$ skutterudite structure.

We performed a Rietveld analysis using the sample prepared at 12 GPa and confirmed that the first iodine-filled skutterudite compound was obtained primarily as a single phase by the high-pressure and high-temperature reaction (Figure 2). The experimental and crystallographic data are listed in Table 1. The refinement was well converged and yielded good R-indices ($R_{wp} = 7.37\%$, $R_I = 4.41\%$, and $R_F = 2.26\%$) as well as a small goodness-of-fit indicator ($S = 1.395$) and no significant impurities were detected.

In the present analysis, iodine is at the center of the Sb_{12} cage (2a site). We examined the off-centered structure model as in $Sn_xPt_4Sn_ySb_{12-y}$, where the guest Sn atoms are not located at the center of the cage but covalently bonded to the host atoms.[31] We checked two off-centered models in which iodine is located in the 48h or 12d site.

Table 1. Crystallographic Data of $I_{0.9}Rh_4Sb_{12}$ and *R* Indices of Rietveld Analysis[a]

formula	$I_{0.9}Rh_4Sb_{12}$
space group	*I m-3* (204)
lattice parameter *a*/Å	9.29997(6)
unit cell volume *V*/Å^3	804.35(1)
2θ range/degree	18−120
R_{wp}/%	7.37
R_P/%	5.69
R_e/%	5.28
R_I/%	4.41
R_F/%	2.26
goodness of fit *S*	1.40

[a] $R_{wp} = [\Sigma_i w_i\{y_i - I_i\}^2/\Sigma_i w_i y_i^2]^{1/2}$ $R_p = \Sigma_i |y_i - I_i|/\Sigma_i y_i$ $R_e = [(N - P)/\Sigma_i w_i y_i^2]^{1/2}$ $R_I = \Sigma_k |I_k(\text{“o”}) - I_k(c)|/\Sigma_k I_k(\text{“o”})$ $R_F = \Sigma_k |[I_k(\text{“o”})]^{1/2} - [I_k(c)]^{1/2}|/\Sigma_k [I_k(\text{“o”})]^{1/2}$ $S = R_{wp}/R_e$; y_i: observed intensity, I_i: calculated intensity, w_i: weight, *N*: number of data, *P*: number of parameters, I_k“o”): estimated observed intensity of the k-th reflection, $I_k(c)$: calculated intensity of the k-th reflection.

Table 2. Structural Parameters *ocp*, *n*, *x*, *y*, *z*, and *B*/Å^2 of $I_{0.9}Rh_4Sb_{12}$

	ocp	*n*[a]	*x*	*y*	*z*	*B*/Å^2
I	0.905(6)	1.81(1)	0	0	0	0.46(9)
Rh	1	8	0.25	0.25	0.25	0.50(6)
Sb	1	24	0	0.34108(8)	0.15507(9)	0.90(5)

[a] *n*, number of equivalent atoms per unit cell.

Our refinement using both models, however, did not work for our compound and no meaningful results were obtained. Therefore, we concluded that the guest is situated at the center of the cage.

The refined atomic parameters and isotropic thermal displacement parameters are listed in Table 2. The thermal displacement parameter of each site was refined individually. The occupational parameter of iodine was also refined in the final refinement stage converging to 0.9, indicating that the calculated composition by the Rietveld analysis was $I_{0.9}Rh_4Sb_{12}$, which corresponds well to the composition of $I_{0.95}Rh_{3.91}Sb_{12}$ determined by EPMA.

We also performed Rietveld analysis of the 5 GPa sample and found that the composition is $I_{0.73}Rh_4Sb_{12}$. The smaller lattice constant (9.2937(1) Å) as compared to that of the 12 GPa sample (9.29997(6) Å) probably reflects the difference of the iodine content.

The structure of $I_{0.9}Rh_4Sb_{12}$ is the same as that shown in Figure 1. In cases of Ln−Co/Fe−Sb filled-skutterudite systems (Ln: lanthanide elements), lattice constants of filled skutterudite compounds often show slightly smaller lattice constants than their mother compounds, $CoSb_3$ and $FeSb_3$. The lattice constants of $Ln_{0.1}Rh_4Sb_{12}$, Ln = La (9.2213 Å)[32] and Yb (9.2289 Å)[33] are also smaller than that of $RhSb_3$ (9.2322 Å). However, the lattice constant of $I_{0.9}Rh_4Sb_{12}$ is larger than that of the mother compound ($RhSb_3$) as mentioned previously. This difference results form the large ionic radii of I^- ions as compared to those of lanthanide ions.

The Rh—Sb bond length of 2.63 Å is almost the same as that in $RhSb_3$ (2.621 Å), indicating that there is no significant change in the binding character of Rh—Sb through insertion of iodine into the skutterudite

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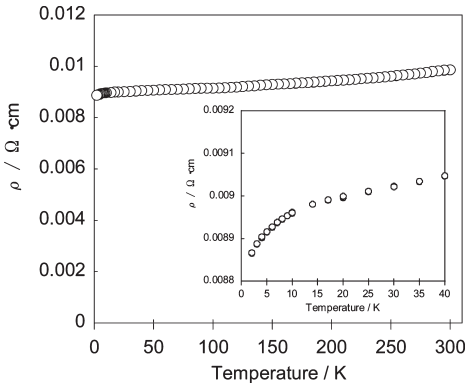

Figure 3. Temperature dependence of the electrical resistivity of $I_{0.9}Rh_4Sb_{12}$.

structure. The Sb—Sb bond lengths of 2.88 and 2.96 Å are longer than those in $RhSb_3$ (2.80 and 2.92 Å),[30] but they are very similar to the Sb—Sb distances in $CoSb_3$ (2.90 and 2.98 Å),[30] $IrSb_3$ (2.85 and 2.95 Å),[30] and $CeFe_4Sb_{12}$ (2.92 and 3.00 Å).[34] The I—Sb distance of 3.48 Å is slightly longer than the A—Sb distances (A: guest ion) in $LaFe_4Sb_{12}$ (3.41 Å)[35] and $BaFe_4Sb_{12}$ (3.46 Å).[36]

Oxidation State of Iodine. In iodine-doped type I germanium clathrate $I_8[Ge_{44}I_2]$, iodine occupies two sites: one is at the center of the cages and the other replaces germanium in the host network.[5] In this germanide, I atoms in the cages are considered to be in the anionic state (I^-). In contrast, I atoms in the host network, which have tetrahedral coordination, are said to be I^{3+} cations. In the case of $I_{0.9}Rh_4Sb_{12}$, all I atoms are at the center of the cages, and the oxidation state is very likely to be I^-. To confirm the oxidation state of I in our sample, we performed X-ray photoelectron spectroscopic (XPS) measurements. The iodine $3d_{2/5}$ state was observed at 619 eV. The values reported for I^- (619 eV) in published data[37,38] confirm that the oxidation state of iodine in the skutterudite cages is I^-. From these observations, we concluded that $I_{0.9}Rh_4Sb_{12}$ is the first filled skutterudite compound having anionic species in the cage.

Electrical and Magnetic Properties and Electrical Structure. The magnetic susceptibility of this compound was too small to measure using the SQUID magnetometer even at 2 K, indicating that this compound is nonmagnetic. The electric resistivity of $I_{0.9}Rh_4Sb_{12}$ gradually decreases as temperature decreases, and below about 10 K, it decreases rapidly to a value of 0.0089 Ωcm at 2 K (Figure 3). However, in short, it is almost constant. The relatively high resistivity at 2 K shows that $I_{0.9}Rh_4Sb_{12}$ is a moderate metallic conductor.

Accounting for the deficiency of iodine is difficult, so we calculated the band structure for a fully occupied structure using the atomic parameters determined by Rietveld analysis. Because the deficiency of iodine is only about 10%, calculation using a stoichiometric model satisfactorily assesses the electrical structure of $I_{0.9}Rh_4Sb_{12}$.

The band structure of IRh_4Sb_{12} in the energy range of −2 to 2 eV is shown in Figure 4(a). One band crosses the E_F on the paths from Γ to H, H to N, and N to Γ. The band structures of $RhSb_3$ and $CoSb_3$ contain a similar band.[39] In these nonfilled skutterudites, the E_F levels are at the top of the single band (Γ point). In contrast, in $LaFe_4Sb_{12}$ the top of the single band goes down and the band gap between the single and the conduction bands increases.[40]

Figure 4(b) shows the contributions from iodine with a fat-band representation. Little contribution of iodine to the conducting electron band is observed. Bands mainly composed of p orbitals of iodine lie below the E_F. These low-lying p orbitals can accommodate electrons from the host network and produce I^- ions.

The total and partial density of states (DOS) of the iodine-filled skutterudite are shown in Figure 5, where the Fermi level (E_F) is set as zero. Two bands are shown: the upper band (> 1 eV) is completely unoccupied, and the E_F lies in the lower band, indicating that the compound has metallic properties. The total DOS shows a small peak near the calculated E_F. The real E_F is very close to the calculated value because total electrons are reduced by only 0.1 electrons per cell. The band around the E_F consists mainly of Rh-p, Rh-d, and Sb-p orbitals, and the contribution of iodine is low.

Comparison of the E_F of IRh_4Sb_{12} to those of $RhSb_3$, $CoSb_3$, $La_{0.5}Co_4Sb_{12}$, and $LaFe_4Sb_{12}$ is meaningful. The DOS plots for these compounds are similar to that of IRh_4Sb_{12}; however, the relative positions of the Fermi levels for $RhSb_3$, $CoSb_3$, and $La_{0.5}Co_4Sb_{12}$ are different.[39−42] Figure 6 shows a schematic diagram of DOS very near to the Fermi levels for these skutterudite compounds. In the pseudogap, one band exists as mentioned previously. This band touches or almost touches the upper band in $RhSb_3$, $CoSb_3$, and IRh_4Sb_{12}.

Counting the total number of electrons accommodated in the host network is helpful for an understanding of the change of E_F. For $RhSb_3$, the number of electrons per Rh_4Sb_{12} unit is $4 \times (9 + 5 \times 3) = 96$. $CoSb_3$ has the same number of electrons per Co_4Sb_{12} unit. For $La_{0.5}Co_4Sb_{12}$, the number of electrons is 97.5, because one La ion donates three electrons to the host network. The increase of the number from 96 results in the higher E_F of $La_{0.5}Co_4Sb_{12}$ compared to that of $CoSb_3$.

The total number of electrons for $LaFe_4Sb_{12}$ is 95 ($= 3 + 8 \times 4 + 5 \times 12$), because one Fe atom has one

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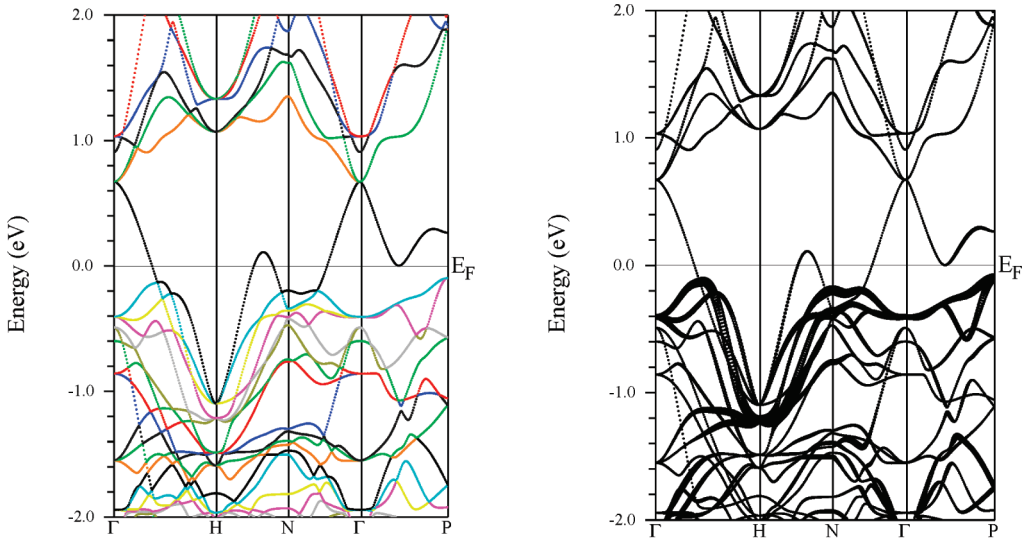

Figure 4. (a) Band structure of IRh_4Sb_{12} for a path along symmetry points of the bcc Brillouin zone over the valence band region. One band crosses the Fermi level. The individual bands are shown in different colors. (b) Band structure for IRh_4Sb_{12} with fat-band representation for I atoms.

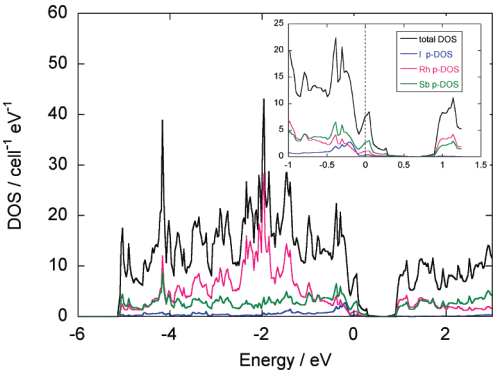

Figure 5. Density of states (DOS) for IRh_4Sb_{12} obtained from LAPW calculations (using Wien2k code). The total DOSs are shown as a black solid line. Partial DOSs are also given as blue, red, and green lines for I, Rh, and Sb, respectively. The Fermi level is set as zero.

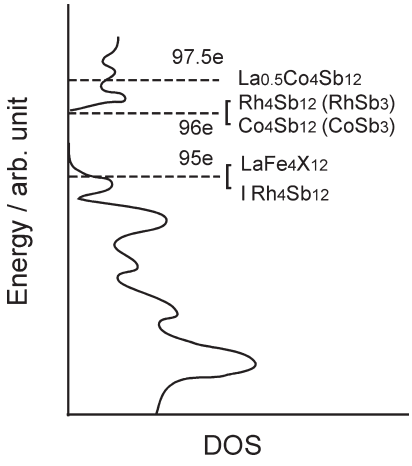

Figure 6. Schematic diagram showing the Fermi energy levels for some skutterudite compounds.

less electron than a Co atom. Therefore, the E_F goes down, and the lower band becomes the conduction band. The position of E_F for $LaFe_4X_{12}$ is very similar to that of IRh_4Sb_{12}, suggesting that IRh_4Sb_{12} also has one less electron than the mother compound, which means that iodine plays the role of an electron acceptor.

This can be also explained by assuming that the formal oxidation states of Rh/Co and Sb are +3 and −1, respectively. The resulting $[Sb^{1-}]_4$ unit can form two covalent bonds and Sb satisfies the octet rule. With the addition of I into the lattice, I acts as an electron acceptor to satisfy its octet, leading to the formation of one hole per I^{-1}. This scenario corresponds well to the oxidation state of iodine (I^-) in $I_{0.9}Rh_4Sb_{12}$.

Conclusions

The first skutterudite compound $I_{0.9}Rh_4Sb_{12}$ containing anionic species in the icosahedral cages was prepared by a high-pressure and high-temperature reaction. The structure and composition were determined by Rietveld analysis and EPMA, confirming that the structure is about 10% deficient in iodide ions in the cage. $I_{0.9}Rh_4Sb_{12}$ is metallic and shows a nonmagnetic property from room temperature up to 2 K. The conducting electron band comprises mainly Sb-p, Rh-p, and Rh-d orbitals; the bands of I-p orbitals, which make limited contributions to conducting electrons, lie beneath the Fermi level.

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Supporting Information Available: A crystallographic information file (cif). This material is available free of charge via the Internet at http://pubs.acs.org.