Filled Skutterudites — Physics and Chemistry of Iron Antimonides of Alkali, Alkaline-Earth, and Rare-Earth Metals

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Introduction

The class of compounds known as "skutterudites" exhibits a wealth of topical behaviors. These materials derive from the mineral Skutterudite ($CoAs_3$) [1]. Binary skutterudites having the general chemical formula TX_3 are formed by the members of the 9th group of the periodic table T = (Co, Rh, Ir) with pnicogens X = (P, As, Sb). No binary compounds with iron, ruthenium, and osmium could be synthesized so far under equilibrium conditions, obviously for electronic reasons. In order to stabilize such compounds it is necessary to include electropositive elements as a third component leading to the formula $M_yT_4X_{12}$ (filled skutterudites [2,3]). Compounds with rare-earth, actinide, and alkaline-earth metals or thallium as cation M were synthesized. Different degrees of filling y can be realized up to $y = 1$, however, the limits for y depend strongly on the cation M and the "host" T_4X_{12} and are not yet well explored. In these filled skutterudites the stabilizing M atoms reside in large voids already present in the T_4X_{12} framework (Fig. 1).

A variety of properties have been observed — mainly for rare-earth filled skutterudites — ranging from metal-insulator transitions to magnetic and quadrupole orderings, conventional and unconventional superconductivity, heavy-fermion/non-Fermi-liquid behavior, and fluctuating/intermediate valency. Furthermore, interest in these compounds is fueled by their possible use in thermoelectric applications [4]. Many studies suggest that the physics of filled skutterudites is governed by a subtle interplay of the filler ions and their surrounding transition-metal pnicogen host structure. However, only a few publications were devoted to the physics of the host.

In order to gain a better understanding of these processes and thus, to explore novel non rare-earth skutterudites, we have successfully synthesized new alkali-metal iron antimonides with sodium and potassium [5]. These light "filler" atoms with *s*-electrons in their conduction bands are not magnetic and, therefore, are a good choice for the investigation of the *d*-electron influence on the structural chemistry and the physical properties of filled skutterudites. Surprisingly, these compounds order ferromagnetically at about 85 K. The basic properties have already been reported [6,7,5]. In contrast, the alkaline-earth (Ca, Sr, Ba) compounds [3,7,8] remain paramagnetic down to 2 K. Nonetheless, our electronic structure calculations within the local density approach (LDA) indicate that the ground states of Ca, Ba, Yb, and $LaFe_4Sb_{12}$ should also be ferromagnetic. Obviously, strong spin fluctuations not described within the LDA destroy the ferromagnetism.

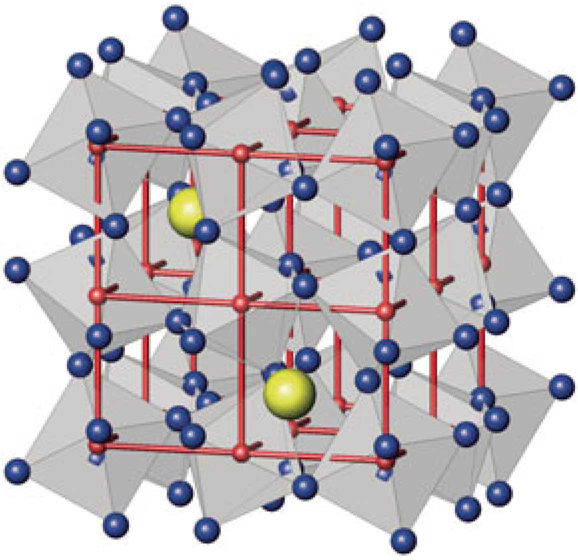

Fig. 1: Cubic unit cell of iron-antimony skutterudites MFe_4Sb_{12} containing two formula units (yellow spheres M = alkali, alkaline-earth, rare-earth metal; red spheres Fe; blue spheres Sb).

Recently [11], we could prove that Yb in $Yb_{1-x}Fe_4Sb_{12}$ is divalent, and that its properties are not caused by the formation of a heavy-electron state, induced by the Kondo effect, at low temperatures as previously claimed. Consequently, the electronic properties of $Yb_{1-x}Fe_4Sb_{12}$, $CaFe_4Sb_{12}$, and $BaFe_4Sb_{12}$ are found to be almost identical. These paramagnetic compounds have a huge Sommerfeld-Wilson ratio ($\approx$ 24 for Yb and Ca) [11], demonstrating that they are situated close to ferromagnetic order. The aforementioned similarity originates from a specific band structure feature at the Fermi level of all three compounds, as found by high-resolution band structure calculations. It is mirrored in their optical properties which were the topic of a recent investigation [12].

A study of the low-temperature specific heat of several filled skutterudite compounds [9] resulted in comprehensive information on the electronic and phononic contributions, in particular on a low-lying Einstein phonon ("rattler") [10] of the weakly bonded filler in these compounds. The temperature dependences observed in the low-temperature electrical resistivity of the Fe-Sb skutterudites are quite different and a topic of current research.

As already mentioned, the suppression of ferromagnetic order in the paramagnetic compounds is largely due to the action of spin fluctuations. This phenomenon was addressed by performing measurements of nuclear magnetic resonance (NMR) and magnetization as well as by electronic structure calculations. Results are reported in [13,14,7]. Our band structure calculations indicate that the ferromagnetic compounds are nearly half-metallic ferromagnets for which a large spin polarization can be expected. We could prove this theoretical conclusion by spectroscopic investigations on point contacts [15].

Chemical Physics of Filled Skutterudites

The preparation of poly- and single crystalline material and the basic crystallographic features of the new compounds $NaFe_4Sb_{12}$ and KFe_4Sb_{12} were already reported in the last *Scientific Report* [5] and in Ref. [6,7,11]. Single crystal X-ray diffraction (XRD) analysis of $NaFe_4Sb_{12}$ corroborates the full occupancy (100%) of the Na. Fe and Sb positions do also not show any deviation from full occupancy. This result is confirmed by WDXS analyses and for KFe_4Sb_{12} [7]. Similar results are obtained for $CaFe_4Sb_{12}$ and $BaFe_4Sb_{12}$, however, for the La and the Yb compound deviations from full occupancy of the filler site were found ($La_{0.79}Fe_4Sb_{12}$ ($x = 0.21$) and $Yb_{0.95}Fe_4Sb_{12}$ ($x = 0.05$)).

At room temperature, all filler atoms in $[Fe_4Sb_{12}]$ skutterudites display a large displacement parameter. Detailed investigations were performed for $NaFe_4Sb_{12}$. Powder neutron diffraction measurements show that the atomic displacement parameter of Na is strongly temperature dependent, while the values for Sb and Fe show only a weak or almost no dependence on temperature. At 2 K, the displacement (U_{iso}) values for all three positions are of similar magnitude close to zero. The difference between the displacement parameters for Na and Fe (Sb) extrapolated to $T = 0$ is less than 0.005 Å^2, which range roughly 3 mean e.s.d. This corresponds to the common thermal motion (Einstein oscillator) of sodium atoms inside the slightly oversized antimony cage. No indications of a lock-in-type phase transition were found. At room temperature, off-center displacements of the sodium atom can be ruled out due to the spherical distribution of the difference electron density in the vicinity of the Na position [7]. The thermal expansion of $NaFe_4Sb_{12}$ was studied by powder XRD down to 15 K. For the temperature range 100–300 K, the linear coefficient of thermal expansion is as low as $\alpha = 11 \times 10^{-6}$ K^{-1} and reveals a rather rigid material. The pressure dependence of the unit-cell volume of $NaFe_4Sb_{12}$ in the range up to 9.5 GPa is typical for intermetallic compounds. The least-squares fit of a Murnaghan-type equation of state to the data leads to a zero-pressure unit cell volume $V_0 = 772.78$ Å^3 and to a bulk modulus $B_0 = 85(1)$ GPa using $B_0' = 4$ [7].

Full occupation of the M position in $NaFe_4Sb_{12}$ and KFe_4Sb_{12} raised the question about the origin of their stability. To get more insight into this topic, the analysis of the chemical bonding with the electron localization function (ELF, η) method was performed. $NaFe_4Sb_{12}$ displays only three types of attractors in the valence region which can be taken as a fingerprint for direct (covalent) atomic interactions (Fig. 2). Two of them are located on the shortest Sb-Sb contacts d_1 and d_2 in the Fe-Sb framework, confirming the covalent character of the interaction between the Sb atoms belonging to neighboring $[FeSb_6]$ octahedra. The third one is located slightly off the Fe-Sb bond lines, showing a pronounced covalency of these bonds, too (Fig. 2b). No unique attractors were found in the valence region between the sodium and framework atoms.

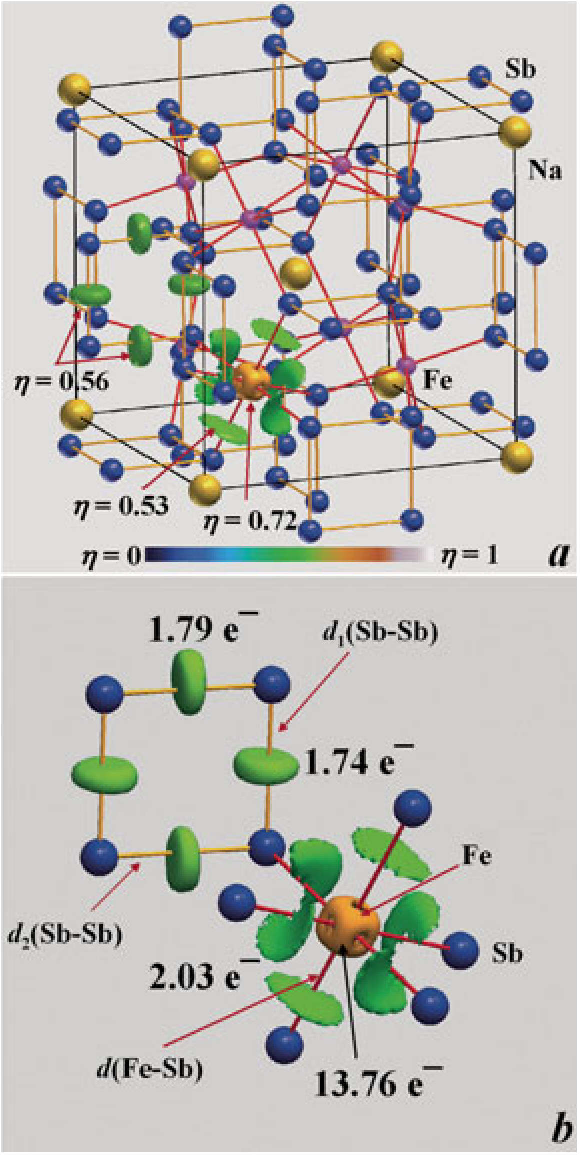

Fig. 2: Electron localization function η for $NaFe_4Sb_{12}$. (a) Crystal structure of $NaFe_4Sb_{12}$ with shortest interatomic distances Fe-Sb and Sb–Sb. Isosurfaces of ELF illustrate the covalent interaction between Fe and Sb ($\eta = 0.53$) and between Sb atoms ($\eta = 0.56$). The isosurface for $\eta = 0.72$ shows the structuring of the third shell for the Fe atoms; see text. (b) Electron counts for relevant bonds in the $NaFe_4Sb_{12}$ structure.

The basins of ELF attractors are defined by zero-flux surfaces in the gradient field of ELF. The lowest ELF values at the interconnect points between two basins indicate the degree of charge separation. The basin of the sodium inner shell interconnects with the framework basin only at a very low value of η (< 0.1). Both facts — the absence of bonding attractors in the vicinity of sodium atoms and the clear charge separation — strongly suggest a charge transfer from sodium to the Fe-Sb framework. Another relevant topological feature of ELF in $NaFe_4Sb_{12}$ is the structuring of the inner shell of the iron atoms (see the isosurface with $\eta = 0.72$ in Fig. 2b). This highlights a participation of the inner-shell electrons of iron in the interactions in the valence region between the atoms. Integration of the total electron density in the ELF basins for the Sb-Sb attractors gives electron counts of 1.74 and 1.79 for d_1(Sb–Sb) and d_2(Sb–Sb), respectively. For the Fe–Sb contacts, a count of 2.03 electrons was obtained (Fig. 2b). In case of the inner shell of the iron atoms, 13.76 electrons were found (14 expected), which is in good agreement with the calculation for free atoms and confirms the participation of the inner-shell electrons in the interactions in the valence region. For the core region of the sodium atoms 9.98 electrons were found from the integration, in good agreement with the value of 10 expected from the Aufbau principle for Na^+. This would give a charge transfer of 1.02 electrons from each Na to the $[Fe_4Sb_{12}]$ polyanion. The polyanion is formed by 6 Sb–Sb (d_1), 6 Sb–Sb (d_2), and 24 Fe–Sb bonds. This yields a total count of 69.90 electrons for the polyanion and results in a charge transfer of 0.94 electrons from each Na to the polyanion [7]. Accordingly, the total electron balance can be written as $Na^{0.98+}[Fe_4Sb_{12}]^{0.98-}$. Considering the strong overlap of the 3*s* band of Na with the Sb 5*p* band in the density of states (DOS) and taking into account the rectangular arrangement of the Sb–Sb bonds in the structure (Fig. 1), we propose a transfer of the sodium charge to the Sb–Sb bonds. Following the ELF representation, the $NaFe_4Sb_{12}$ structure has to be considered as a three-dimensional covalently bonded polyanionic framework of Fe and Sb atoms with Na cations embedded into the cavities. This scenario is in agreement with the large rigidity of the structure.

Thermal Properties — Electronic and Structural Dynamics

As already mentioned, the prominent structural feature of the filled skutterudites is the unique crystallographic position of the cation in an oversized icosahedral void formed by pnicogen atoms. This leads to anomalously large displacement parameters of the "filler" cation, a thermal motion commonly termed "rattling". The phonon-dominated thermal conductivities of filled skutterudites are roughly an order of magnitude smaller than those of its unfilled equivalents [4,10]. The mechanism of the suppression of the thermal conduction by the "rattler" is not yet fully understood [10]. It is also unclear whether this thermal motion is mostly harmonic or implies a multi-well potential and, eventually, a structural lock-in transition at low temperatures. The availability of filled skutterudites with cations of atomic mass spread between *ca.* 23 (Na) and 173 (Yb) offered the possibility to obtain more information on the "rattler", its influence on transport properties and its interplay with electronic degrees of freedom.

In the following we will present an analysis of the contributions to the specific heat $c_P(T)$ of skutterudites with $[Fe_4Sb_{12}]$ host [9]. For temperatures above 100 K the values of $c_P(T)$ for M = Na, K, Ca, and $La_{0.79}$ are almost identical. The data for the compounds with M = Na, K display a small second-order anomaly at T_C = 81 K (transition midpoint, M = Na) and 80 K (M = K), respectively, with widths below 1% of T_C, in good agreement with the Curie temperatures determined from magnetization measurements [7].

Figure 3 displays the low-temperature specific heat below 14 K. It is obvious that the electronic terms γT for the compounds with Na, K, Ca, and Ba are of the same size (γ = 100–120 mJ mol^{-1} K^{-2}). Only for very low temperatures, $c_P(T)$ can be fitted by a simple model $c_P(T) = \gamma T + \beta T^3$ including the linear electronic Sommerfeld term and the Debye T^3 lattice term. In order to account for the thermal exitation of the loosely bonded cation, an Einstein term (characteristic temperature Θ_E) for the atom on this site needs to be combined with the Debye model (Debye temperature Θ_D) for the remaining atoms of the polyanion. The specific heat at low temperatures is fitted by $c_P(T) = \gamma T + \beta T^3 + \delta T^5 + \varepsilon E(T / \Theta_E)$ where β contains the initial Debye temperature $\Theta_D(0)$, and E is the Einstein function. The Debye contribution δT^5 is already of importance for temperatures at which the Einstein term becomes significant. This model is not expected to work at higher temperatures where optical phonon modes of the $[Fe_4Sb_{12}]$ host need to be taken into account. Also, the contributions to $c_P(T)$ of $La_{1-x}Fe_4Sb_{12}$ cannot be analyzed on the basis of zero-field data due to the presence of a strongly field-dependent spin fluctuation contribution [9].

Fits where both δ and ε were allowed to vary were found to be of limited use since there exists a strong numerical anti-correlation of δ with ε [9]. We therefore neglected the Debye T^5 term ($\delta = 0$) which is a useful approximation for $T/\Theta_D(0) < 0.05$. The obtained parameters agree with alternative fits for which ε was fixed to $3R$ (R = molar gas constant) multiplied by the cation filling factor [9]. For the light cations M = Na, K, the agreement is excellent while for M = Ca, Ba, and La slightly larger values ε are found. Only for M = Yb a minor impurity (Yb_2O_3 phase) hampers the exact determination of γ, Θ_D, ε, and Θ_E. As an example, a fit and its individual contribution are shown for the $CaFe_4Sb_{12}$ data in Figure 4.

The Sommerfeld coefficient γ of the electronic specific heat of the Na, K, Ca, and Ba compounds range from 98 to 116 mJ mol^{-1} K^{-2}. Also,

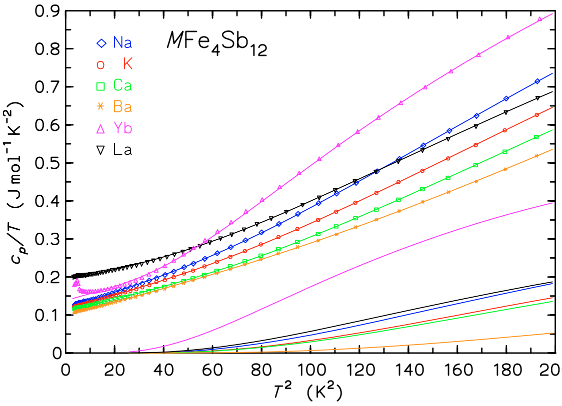

Fig. 3: Specific heat capacity of filled skutterudites MFe_4Sb_{12} (M = Na, K, Ca, Ba, $La_{0.79}$, $Yb_{0.95}$) below 14 K in a c_P/T vs. T^2 representation. The lines show the fits of the model described in the text.

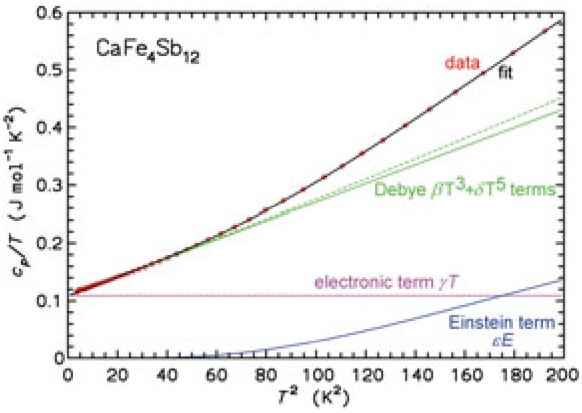

Figure 4: Specific heat capacity of $CaFe_4Sb_{12}$ below 14.1 K. The lines give the contributions of the individual terms of the fit to the model (see text).

$Yb_{1-x}Fe_4Sb_{12}$ shows a value in this range, fully consistent with the large similarities in the electronic density of states (DOS) at E_F [7,11]. Interestingly, only the intrinsic γ of the skutterudite with the trivalent La-ion (effective charge $3(1-x)$) is significantly different, even after considering the strong spin fluctuation contribution [9,16,18].

The initial Debye temperature $\Theta_D(0)$ increases with the charge of the cation from 243 K (Na) to 267 K (Ca) and 274 K (La) indicating an increasingly covalent bonding within the $[Fe_4Sb_{12}]^{-z}$ polyanion structure with increased charge *ze* transferred to it from the cation. A slight decrease of $\Theta_D(0)$ with increasing atomic mass of the cation is observed for the divalent cations Ca, Ba, and Yb. This might indicate a weak coupling of the filler vibrations to the host lattice acoustic phonon modes, i.e., the two phonon systems cannot be treated as totally independent, even at low temperatures.

The Einstein temperatures Θ_E are between 62 K and 104 K. The values can be compared with those derived from diffraction investigations, inelastic neutron scattering, EXAFS, or nuclear inelastic scattering Mössbauer investigations. For example, for M = La the value of Θ_E is available from several methods: a calculation by Feldman *et al*. [19] gives 7.1 meV (82 K), inelastic neutron scattering by Viennois *et al*. [20] yields 7 meV (81 K) for La_{1-x} and a fit to the higher-temperature heat capacity by Sales *et al*. [4] results in 79 K, in good agreement with our value (77 K) for a sample with La_{1-x}.

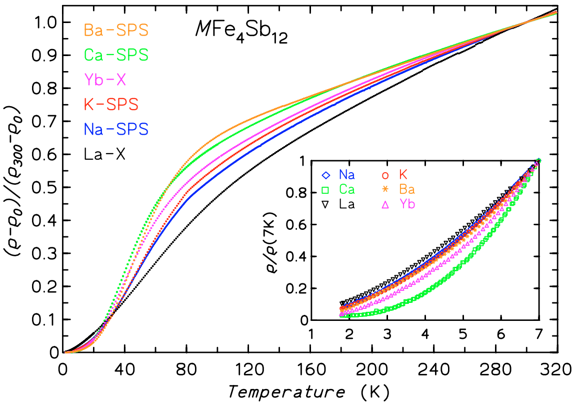

Fig. 5: Normalized electrical resistivity of filled skutterudites MFe_4Sb_{12} (M = Na, K, Ca, Ba, La_{1-x}, Yb_{1-x}). X assigns single crystal samples (La, Yb), all other samples are spark plasma sintered (SPS) material. The inset shows data below 7 K.

Electrical Resistivity and Magnetoresistance

The normalized electrical resistivity $(\rho(T) - \rho_0)/\rho(300\ K)$ of differently prepared compact samples of the six skutterudites is given in Figure 5 [9]. Here, the bulk density of the samples has a very strong influence on the absolute resistivity and the residual resistivity. However, the common feature of the normalized $\rho(T)$ curves is a shoulder around 70–100 K. Such a change of slope at elevated temperature is often due to *s*-*d* scattering, where light charge carriers are scattered off more heavy electrons forming a narrow band near E_F. The shoulder is most pronounced for MFe_4Sb_{12} with divalent cations M. In addition, for M = Ba it is found at a higher temperature compared to M = Ca, Yb. The shoulder has vanished for $La_{1-x}Fe_4Sb_{12}$. In the ferromagnetic Na and K compounds the shoulder is overlaid by the small phase transition anomaly at — most remarkably — the same temperature (Curie temperature $T_C \approx 80$ K). It is likely that the ferromagnetic ordering and the shoulder originate from the same band structure feature near E_F [9].

The inset of Figure 5 shows the low-temperature behavior of the normalized resistivity in zero magnetic field [9]. Again, a clear distinction between the skutterudites with monovalent, divalent, and trivalent cations can be made. $\rho(T, H)$ was fitted by T-power laws with exponent α (plus $\rho_0(H)$) for temperatures up to 7 K. A surprisingly stable power-law behavior is the $T \propto T^{1.9}$ dependence found for the ferromagnetically ordered Na and K compounds, α is even stable up to 20 K and increases from 1.9 in zero field to 2.0 with H = 9 T. This exponent is reminiscent of the common Fermi liquid T^2 dependence while the compounds are ferromagnetic. In contrast, the nearly ferromagnetic compounds (Ca, Yb) display much larger values of α. Most interestingly, for $CaFe_4Sb_{12}$ a high exponent $\alpha \approx 3$ is essentially stable for fit intervals with high limits from 7 K up to 20 K. The Ba compound shows almost the same α as the Yb compound. The values of α, obtained from $\rho(T, H)$ of all three compounds, however, strongly decrease with increasing magnetic field and recover the usual T^2 dependence in a wide temperature interval. The $La_{1-x}Fe_4Sb_{12}$ sample displays strongly different exponents α of 1.61–1.68 (in zero field) — close to $T^{5/3}$, the typical value for ferromagnetic spin fluctuations — and no shoulder at higher temperatures. With increasing field α tends to higher values but the T^2 law is clearly not achieved for $H = 90$ kOe.

The ratio A/γ^2 (where A is the coefficient of the T^2 in $\rho(T)$) in zero field can only be calculated for $NaFe_4Sb_{12}$ and KFe_4Sb_{12}. The resulting values for $T < 7$ K (3.68×10^{-8} and 1.75×10^{-8} Ωm (mol K/J)^2, respectively) [9] are significantly smaller than the common value of $\approx 1\times10^{-7}$ Ωm (mol K/J)^2, indicating that electron-electron scattering is not dominating in the ferromagnetically ordered phase. Turning now to the data taken at $H = 90$ kOe, we find A/γ^2 values of 3.67 for Na, 1.30 for K, 2.38 for Ca, 0.88 for Yb_{1-x}, and 1.63×10^{-8} Ωm (mol K/J)^2 for $La_{1-x}Fe_4Sb_{12}$, respectively. Since just the lower bound of the resistivity and A values seem to be intrinsic, it can be concluded that the ratio A/γ^2 of all MFe_4Sb_{12} is about 10^{-8} Ωm (mol K/J)^2, i.e., one order of magnitude below the so-called Kadowaki-Woods ratio for most (enhanced and heavy) Landau-Fermi liquids. Further investigations are currently underway.

Occurrence of Ferromagnetism in Fe-Sb Skutterudites

The magnetic properties of the filled skutterudites MFe_4Sb_{12} are summarized in Figure 6. All paramagnetic susceptibilities can be approximated by a Curie-Weiss law. The appearance of this temperature dependence of $\chi(T)$ is not due to localized magnetic moments but to spin fluctuations of itinerant (3*d*) electrons [21]. Interestingly, the compounds with alkali and alkaline-earth metals display almost the same paramagnetic moment of 1.5 to 1.7 μ_B/Fe-atom. While for the ferromagnets — as expected — the Weiss temperature Θ is positive and close to the Curie temperature, the paramagnetic isomorphic compounds show lower, but still positive values for Θ. The dimensionless Sommerfeld-Wilson-ratio ($\propto \chi_0/\gamma$, where χ_0 is the low-T plateau value of $\chi(T)$ and γ the Sommerfeld coefficient of the electronic specific heat) is very high (around 24), indicating that these compounds (especially the Ca and Yb-filled ones) are close to a ferromagnetic instability. Only $La_{1-x}Fe_4Sb_{12}$ with $x = 0.21$ (filled with 0.79 La^{3+} cations, i.e. max. 2.37 transferred electrons) displays a significantly lower paramagnetic effective moment (1.2 μ_B/Fe-atom) and a negative Weiss temperature $\Theta = -50$ K.

The occurrence and stability of ferromagnetism in the filled skutterudites with the $[Fe_4Sb_{12}]$ host has been investigated by FPLO band structure calculations using the fixed spin moment (FSM) approach. The FSM method calculates the total energy and the electronic structure for a given, fixed magnetic moment. For M = Na, K (Fig. 7, lower curves), the calculations result in a ferromagnetic ordering with an energy gain of about 0.05 eV (2 mHartree) per unit cell. This energy gain is large enough to overcome the strong spin fluctuations present in MFe_4Sb_{12}. For M = Yb, Ca, Ba this energy gain is considerably smaller (Fig. 7, middle curves). Therefore, strong ferromagnetic spin fluctuations impede the magnetic order for these compounds. In an external magnetic field, these fluctuations are suppressed. From our calculations, we predict a metamagnetic transition for the skutterudites with a

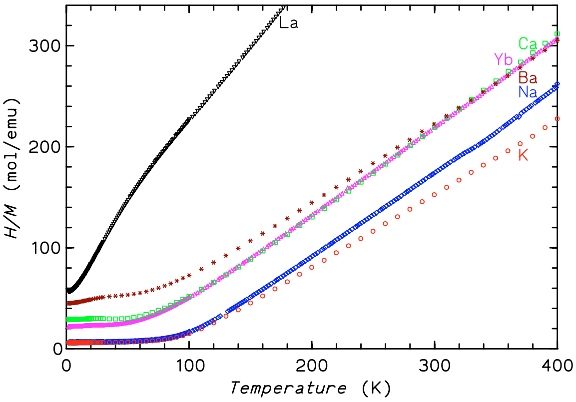

Fig. 6: Inverse magnetic susceptibility H/M(T) of filled skutterudites MFe_4Sb_{12} with various cations M = Na, K, Ca, Ba, La, Yb.

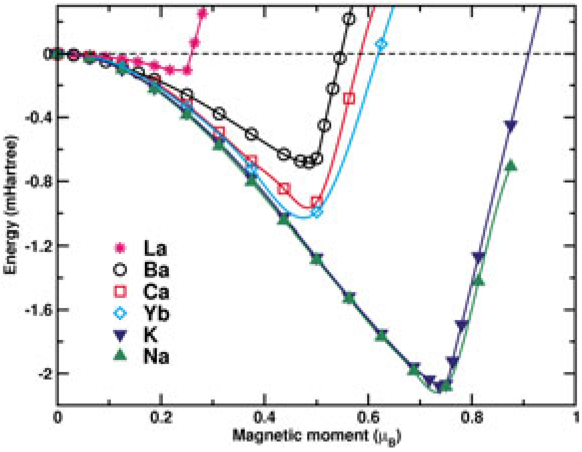

Fig. 7: Relative energy vs. magnetic moment per Fe-atom resulting from fixed spin moment (FSM) calculations for various filled skutterudites MFe_4Sb_{12} (M = Na, K, Ca, Ba, La, Yb; 1 Hartree ≈ 27.2 eV).

divalent filler. According to the FSM calculations, with increasing magnetic field a transition to a ferromagnetically ordered state is predicted in the sequence Yb, Ca, Ba. Recently, this metamagnetic transition has been observed experimentally for M = Ca, Sr, Ba [22], for M = Ca already at $H_{\text{ext}} \approx$ 140 kOe and at higher fields for M = Sr and Ba. For M = La, the energy gain from ferromagnetic ordering is rather small. Thus, a metamagnetic transition is unlikely or could be expected only at extremely high fields.

Magnetic Resonance Studies on Fe-Sb Skutterudites

In the last *Scientific Report* [5] it was shown that the magnetic resonance (NMR/NQR) on the ^{23}Na (I = 3/2) and ^{121,123}Sb (I = 5/2, I = 7/2) nuclei is a powerful local probe to study the magnetism as well as to obtain information about the local symmetry at the nuclei sites of $NaFe_4Sb_{12}$ [23]. Further ^{23}Na-NMR investigations on the solid solution $(Na_{1-x}Ca_x)Fe_4Sb_{12}$ confirm the intrinsic nature of the ferromagnetic transition at 85 K [24]. Comparative NMR and NQR studies on Fe-Sb skutterudites with monovalent (Na), divalent (Ca, Ba) and trivalent (La) filler ions were performed. The ^{121,123}Sb-NQR study combined with *ab-initio* linearized augmented plane-wave calculations provides microscopic evidence for disorder on the filler site [13]. This is also confirmed by ^{23}Na- and ^{139}La-NMR investigations. One scenario to explain the NMR results is based on the presence of intrinsic vacancies existing in the structure [13].

The comparison of the NMR results of the filler ions Na^{1+}, Ba^{2+} and La^{3+} demonstrates the different character of the magnetic correlations in terms of Moriya's self-consistent renormalization theory [21] for itinerant magnets [14]. The spin lattice relaxation rate ($1/T_1$) of ^{139}La in $La_{1-x}Fe_4Sb_{12}$ exhibits a $T^{1/2}$ temperature dependence, which is a unique feature of weakly and nearly antiferromagnetic metals, whereas in $NaFe_4Sb_{12}$ ^{23}Na-($1/T_1$) is well described by the spin-fluctuation theory for itinerant ferromagnets in the ferro- and paramagnetic state ($1/T_1$ proportional to T^1 below T_C, Fig. 8). NMR distinguishes two types of itinerant magnetism: ferromagnetic order in $NaFe_4Sb_{12}$ and weak antiferromagnetic fluctuations in $La_{1-x}Fe_4Sb_{12}$. $BaFe_4Sb_{12}$ seems to be just at the border between dominating ferromagnetic and antiferromagnetic correlations. In this compound, $1/T_1$ was obtained from ^{137}Ba-NQR, where two lines of ^{137}Ba have been found (ν_1 = 45.9 MHz and ν_2 = 49.0 MHz at T = 77 K).

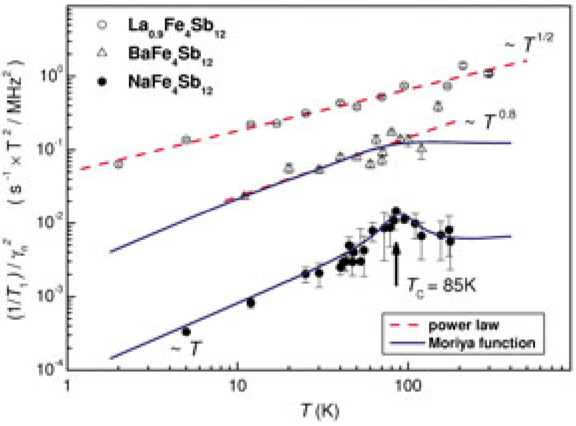

Figure 8: $1/T_1$ normalized to the nuclear gyromagnetic ratio $\gamma_N{}^2$ as a function of temperature as obtained from ^{139}La-NMR ($^{139}\gamma_N$ = 6.014 MHz/T), ^{137}Ba-NQR ($^{137}\gamma_N$ = 4.731 MHz/T, from the ν_{1-} line) and ^{23}Na-NMR ($^{23}\gamma_N$ = 11.262 MHz/T). The solid line is a calculation of $1/T_1$ vs. T based on Moriya's theory [21], making use of the field- and temperature-dependent magnetization M(H,T) for weak itinerant ferromagnets. The dashed line is a fit to a $T^{1/2}$ power law.

A Pseudogap from Iron States

For the compounds MFe$_4$Sb$_{12}$ (M = Ca, Ba, Yb) we performed investigations of their optical electronic excitations. These are characterized by a low-energy pseudogap structure, very similar for each compound, which could nicely be explained by highly accurate LDA electronic band-structure calculations. The Fe-3*d* states generate the observed pseudogap whose characteristics appears to be very similar to the so-called Kondo-insulator gap found in some 4*f* strongly correlated electron systems.

We have measured the near normal incidence optical reflection on MFe$_4$Sb$_{12}$ (M = Ca, Ba, Yb) in a wide spectral region (7 meV – 30 eV) at temperatures 2 K – 300 K [12]. As high accuracy for the reflection data was required, the polycrystalline samples were coated *in-situ* with gold and then used for measuring the reference spectra. After Kramers-Kronig transformation of the reflectivity, the dissipative part of the optical conductivity $\sigma_1(\omega,T)$ was obtained.

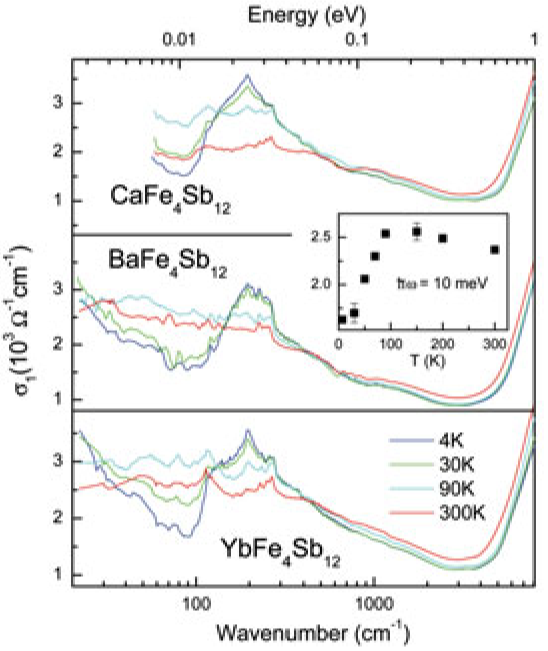

Fig. 9: Spectra of the optical conductivity $\sigma_1(\omega,T)$ at selected temperatures below and above $T \approx 90$ K, where a pseudogap forms below ≅ 17 meV. For $BaFe_4Sb_{12}$ the inset shows $\sigma_1(\omega,T)$ at $h\omega = 10$ meV, demonstrating the evolution of the pseudogap.

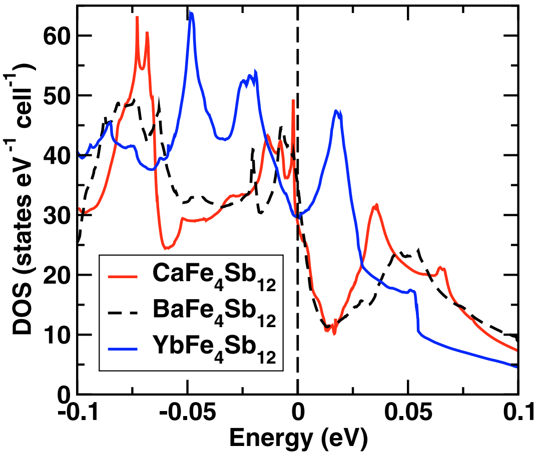

Fig. 10: Total density of states of MFe_4Sb_{12} near the Fermi level E_F. For M = Yb, the scalar relativistic result is shown without spin-orbit coupling. For M = Ca, Ba the spin orbit coupling was included leading to an upward shift as well as to a broadening of the peak ≈50 meV above E_F.

The compounds show conventional metallic behavior in the optical conductivity $\sigma_1(\omega,T)$ above $T \approx 90$ K whereas for $T < 90$ K it is continuously suppressed until it reaches a minimum value at the lowest temperature. This behavior of $\sigma_1(\omega,T)$ and its enhancement for energies between 17 and 60 meV indicates the formation of a pseudogap in the electronic charge excitations below ≅ 17 meV (Figure 9).

Remarkably, all investigated compounds MFe$_4$Sb$_{12}$ (M = Yb, Ba, Ca) show a very similar pseudogap behavior of their optical conductivities, pointing towards a very similar electronic band-structure.

To obtain accurate electronic structure information (Fig. 10), a full potential, non-orthogonal local-orbital calculation scheme within L(S)DA was used. For M = Ca, Ba, calculations including spin-orbit coupling were performed whereas for M = Yb the LDA+U scheme was applied. To ensure accurate band structure and density of states we used for the fully relativistic calculations a very fine mesh of 5551 points in the irreducible part of the Brillouin zone. The optical pseudogap and its different appearances in BaFe$_4$Sb$_{12}$ and CaFe$_4$Sb$_{12}$ as well as the sharp features are very well reproduced by our high-resolution LDA band-structure calculations (*cf.* Figs. 9 and 10; [12]). Therefore, at least for MFe$_4$Sb$_{12}$ with M = Yb, Ca, Ba only weak electronic correlations within the Fe3d-Sb5p bands seem to be present. This is a completely different mechanism than the Kondo-insulator gap scenario for 4f heavy-fermion compounds leading, surprisingly however, to similar optical spectra.

Half Metallicity of Ferromagnetic Filled Skutterudites

For the ferromagnetically ordered filled skutterudite NaFe$_4$Sb$_{12}$, band-structure calculations within the local spin density approximation (LSDA) predict a spin-split density of states with almost perfect half-metallic behavior [7]. A material with such electronic properties is considered to be useful for electronic devices based upon spin control (spintronics). Consequently, new materials with a high degree of spin polarization have evolved as topics of particular attention in recent years [25]. In order to verify this prediction experimentally, point-contact Andreev reflection (PCAR) measurements were conducted on KFe$_4$Sb$_{12}$ and NaFe$_4$Sb$_{12}$ samples [15]. Obviously, the two compounds introduce a new class of materials that exhibit a large degree of spin polarization and itinerant electron magnetism with a rather high Curie temperature T_C of 80 K – 85 K.

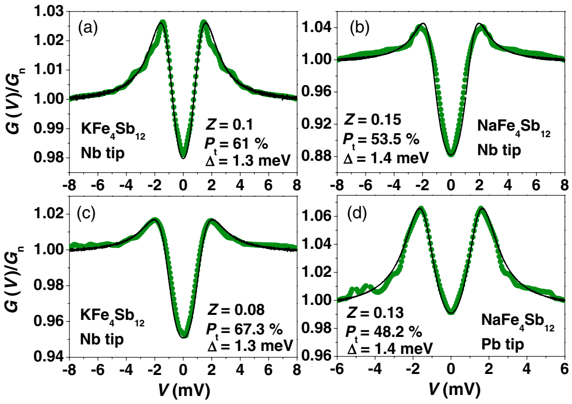

Fig. 11: Selected conductance spectra G(V) for the skutterudites KFe_4Sb_{12} (a,c) and $NaFe_4Sb_{12}$ (b,d) taken at 2.8 K. The spectra were measured (dots) using (a-c) Nb or (d) Pb tips and were normalized to the normal state conductance G_n at high voltage. The lines present the results of the best fits with the fit parameters given in each panel (see text).

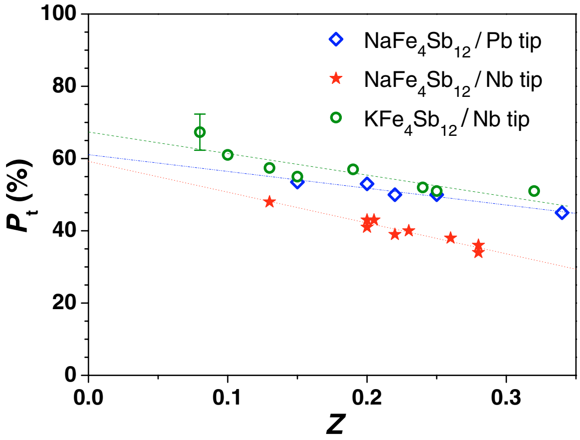

Fig. 12: Transport spin polarization P_t in dependence on the Z-value for the different sample/tip combinations measured. The extrapolation to zero Z yields the intrinsic spin polarization of the two skutterudites. The indicated error bar is representative for all measurements.

The PCAR measurements were performed at 2.8 K on finely polished polycrystalline sample surfaces. Mechanically cut sharp Nb or Pb tips were engaged onto the samples to establish contacts of minimum area. Differential conductance $G(V)$ versus voltage V characteristics of the contacts were recorded. The typical resistance of the contacts in the normal state varied between 10–20 Ω. This, combined with the sharp double maxima structure in the G–V spectra, symmetric about $V = 0$, may point towards a ballistic nature of the point-contacts. In Figure 11 we show four representative spectra. The transport spin polarization P_t was extracted by fitting the spectra with a Blonder-Tinkham-Klapwijk (BTK) formula modified to incorporate the effect of spin polarization. The vast majority of spectra could be analyzed using only three fitting parameters, namely P_t, the superconducting energy gap Δ of the tip, and the barrier parameter Z which characterizes the strength of the potential barrier at the interface. Here, the comparatively low Z values of these spectra ensure a good quality of the fits. Note, that those spectra with lowest Z values have the highest impact on the extrapolated intrinsic P_t values.

Figure 12 shows the variation of the extracted values of P_t as a function of the barrier parameter Z. P_t decreases with increasing Z, a behavior that has been observed earlier in a variety of ferromagnets and is believed to arise from spin depolarization at a magnetically disordered scattering barrier formed at the interface. The *intrinsic* value of P_t is therefore extracted by linearly extrapolating the P_t *vs.* Z curve to $Z = 0$. The consistency of this procedure is easily seen in the case of $NaFe_4Sb_{12}$: measurements carried out with both Pb and Nb tips result in the same value of the intrinsic spin polarization (within experimental errors), though the decay of P_t with Z is different for the two cases due to differences in the nature of the interfaces. The intrinsic value of P_t extracted in this way is 67% for KFe_4Sb_{12}, and 60% for $NaFe_4Sb_{12}$. PCAR measurements were also conducted on $CaFe_4Sb_{12}$ and $P_t = 0$ was found for all fitting attempts as to be expected for a non-ferromagnetic material.

To gain further insight into the electronic structure of these materials on a microscopic level, a full-potential, non-orthogonal local-orbital calculation scheme (FPLO) within the LSDA was utilized. Our band structure calculations result in a ferromagnetic ground state for KFe_4Sb_{12} with a nearly integer magnetic moment of 2.98 μ_B per formula unit. The states in the spin-split region originate predominantly from Fe-3*d* hybridized with the Sb-5*p* states. We find an almost fully polarized DOS at the Fermi level E_F for KFe_4Sb_{12} (Figure 13). The DOS contribution in the spin-up channel can be assigned mainly to two bands (Fermi surfaces) of almost pure Fe-3*d* character (Figure 13a). There is only one band of strongly mixed Sb 5*p*–Fe 3*d* character crossing E_F in the spin-down channel (Figure 13a). Due to its high value of the Fermi velocity $v_F \approx 0.3 \times 10^6$ m s^{-1}, this band makes only a tiny contribution to the number of states at E_F. The corre-

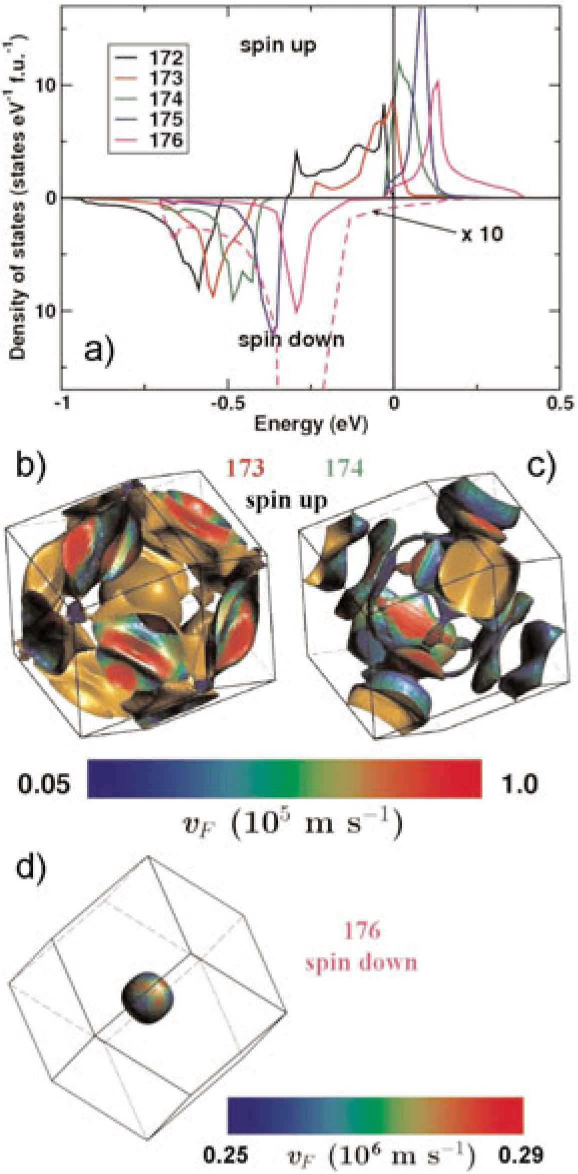

Fig. 13: Calculated density of states (DOS) and Fermi surfaces for KFe_4Sb_{12}. (a) DOS resolved for the individual bands relevant at E_F. Spin-down band 176 has a non-vanishing DOS at E_F (cf. dashed line that represents a factor of 10 magnification). (b,c) Fermi surfaces for the most contributing spin-up bands 173 (b) and 174 (c). The color coding indicates the Fermi velocities v_F. (d) Fermi surface and velocity for the relevant spin-down band 176.

sponding Fermi surfaces, colored according to v_F values, are given in Figure 13b,c and 13d for the relevant spin-up and spin-down bands, respectively. The band structure calculations result in spin polarizations P_t of 99.6 % for KFe_4Sb_{12}, and 99 % for $NaFe_4Sb_{12}$. These calculated values are significantly larger than the measured ones: 67 % and 60 %, respectively.

In case of spin polarization measurements it is imperative to bear in mind that in addition to the DOS at E_F, $N(E_F)$, also the Fermi velocity v_F may influence the obtained value. From the band structure calculations we find very different v_F for the two spin channels (Fig. 13). As a result, the calculated spin polarization is reduced in the skutterudite materials in which the high value of P_t stems from the almost completely spin-polarized DOS at E_F. The opposite behavior is found in so-called transport half metals (e.g., the manganites) in which the high values of the transport spin polarization P_t are mainly due to extremely different values of v_F.

We note that the spin polarization as obtained from band-structure calculations does not include several factors which are detrimental to a large transport spin polarization. First, the weak itinerant ferromagnetic nature of the filled skutterudites is associated with large spin fluctuations [6,7] which may reduce the spin polarization from its theoretical value. The presence of strong ferromagnetic fluctuations in these compounds was already indicated above. Note that the high field magnetization value (when spin fluctuations are quenched) is the one that corresponds to band structure calculations. Hence, a crude correlation between magnetization and spin polarization would suggest a 50 % decrease in the spin polarization arising from this effect alone. Second, it has been seen in several compounds that P_t of the surface can be reduced with respect to its bulk value. In addition, spin-orbit coupling in the ferromagnet would also reduce the spin polarization at the Fermi level. Third, our contacts might not be in the pure ballistic regime. From the band-structure calculations, the expected spin polarization is $P_1 = 0.968$ for a contact in the ballistic regime and $P_2 = 0.765$ in case of a purely diffusive contact putting emphasis on the actual nature of the contact in our PCAR measurements. Considering these factors, the observation of 67 % spin polarization in KFe_4Sb_{12} is indeed surprising. The key to robustness of the transport spin polarization against these detrimental effects may indeed lie in the fact that P_t in this material is primarily governed by the density of states (rather than the Fermi velocity) of the majority (spin-down) channel, which is very small over a relatively large energy range close to E_F. This renders P_t less sensitive not only to fluctuation effects but also with respect to impurity scattering, an aspect which is of importance to realize its application potential.

Summary

In our detailed study of the Fe-Sb-based skutterudites, stabilized by non-magnetic cations, interesting aspects and consequences of the electronic properties of the host structure could be unraveled. One particular point is the occurrence of weak band ferromagnetism when transferring one electron to the $[Fe_4Sb_{12}]$ host by incorporation of Na^+ and K^+ ions. Strong spin fluctuations destroy this ground state in compounds with Ca^{2+}, Sr^{2+} and Ba^{2+} ions, whereas in case of trivalent filler ions (e.g. La^{3+}) antiferromagnetic spin fluctuations become dominant. Exceptional agreement between band structure calculations and experiments could be achieved. This is demonstrated by the confirmation of the temperature-dependent optical band pseudogap found in $CaFe_4Sb_{12}$ (and in the isoelectronic Ba and Yb compounds) by high-resolution LDA calculations. Moreover, the ferromagnetic Na and KFe_4Sb_{12} compounds were predicted by LDA calculations to be nearly half-metallic ferromagnets. This interesting property could be experimentally proofed by measuring a large transport spin polarization by point contact spectroscopy.

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