**TlFe$_4$Sb$_{12}$: A weak itinerant ferromagnetic analogue to alkali-metal iron-antimony skutterudites**

A. Leithe-Jasper,* W. Schnelle, H. Rosner, R. Cardoso-Gil, M. Baenitz, J. A. Mydosh,† and Yu. Grin

*Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany*

M. Reissner and W. Steiner

*Institut für Festkörperphysik, Technische Universität Wien, Wiedner Hauptstraße 8–10, 1040 Wien, Austria*

**Abstract**

Structural, thermal, electronic, and electrical transport properties as well as high-field $^{57}$Fe Mössbauer investigations are reported for the new compound TlFe$_4$Sb$_{12}$ in which thallium attains the formal valency of +1. Similar to the isostructural NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ homologues the Tl-filled skutterudite is an itinerant ferromagnet with small ordered moment below $T_C = 80$ K. The electronic structure calculated by density functional methods exhibits a band-ferromagnetic groundstate and nearly half-metallic properties. The specific heat is dominated by a low-lying mode due to vibrations of the Tl cation in the cavity of the [Fe$_4$Sb$_{12}$] polyanionic host. Electrical resistivity displays a characteristic hump and a sharp anomaly at $T_C$. These features and the large magnetoresistance at low temperatures can be explained by a strong compensation of hole and electron carriers in the band structure. Temperature-dependent $^{57}$Fe Mössbauer spectroscopy confirms the magnetic order and its character.

PACS numbers: 75.50.Bb, 75.40.Cx, 76.30.Fc
I. INTRODUCTION

Recently, we have shown by experimental and theoretical investigations that filled skutterudites MFe$_4$Sb$_{12}$ with the alkali metals sodium and potassium as M component (“filler”) represent a new class of itinerant weak ferromagnetic half-metals.$^{1-3}$ In these compounds the alkali metals donate one electron to the iron-antimony [Fe$_4$Sb$_{12}$] framework (“host”) which gives rise to the stabilization of a highly spin-polarized$^3$ ferromagnetic ground state below $T_C \approx 80$ K. In contrast, transfer of more than one electron by other cations results in paramagnetic ground states with strongly enhanced susceptibilities at low temperatures.$^{2-7}$ Compounds with divalent cations are nearly ferromagnetic metals.$^{2,5-7}$

In their systematic studies of thermoelectric properties of filled skutterudites based on CoSb$_3$ Sales et al.$^8$ synthesized and characterized the compounds Tl$_x$Co$_4$Sb$_{12}$-$y$Sn$_y$ and Tl$_x$Co$_{4-y}$Fe$_y$Sb$_{12}$ with Tl contents up to $x = 0.8$.$^{9-11}$ Mainly the thermal and electrical transport properties as well as the phonon spectra of these material were investigated. The strong decrease of the thermal conductivity with increasing thallium content was attributed to localized incoherent vibrations of the Tl filler (“rattling”). A corresponding, remarkably low-lying Einstein mode ($\Theta_E = 53$ K) was observed both in the low-temperature specific heat as well as a peak in inelastic neutron scattering experiments.$^{9,11}$

These findings and the fact that thallium can be stabilized with an oxidation state of +1, where it should show many similarities with the alkali metals,$^{12}$ prompted us to synthesize the compound TlFe$_4$Sb$_{12}$ which represents a new skutterudite completely based on iron as a 3$d$ metal. In contrast to Co-based skutterudites,$^{9-11}$ in the new compound nearly all icosahedral voids are filled with thallium. An interesting aspect is the large mass of the Tl$^+$ cation compared to the other monovalent fillers (Na$^+$ and K$^+$) which have until now successfully been “inserted” in the [Fe$_4$Sb$_{12}$] polyanion.

In this work we show the results of magnetization, electrical resistivity, magnetoresistance, Hall effect, heat capacity, and high field $^{57}$Fe Mössbauer measurements as well as detailed electronic structure calculations. TlFe$_4$Sb$_{12}$ has – like its Na and K homologues – a ferromagnetic ground state with $T_C = 80$ K and a nearly half-metallic band structure with a high density of states at the Fermi level. Similar to the above-mentioned Co-based skutterudites a low-lying vibrational mode of the Tl cations in the host lattice is observed and analyzed.
II. EXPERIMENTAL

The synthesis of TlFe$_2$Sb$_{12}$ is similar to that of alkali-metal filled skutterudites.$^2$ First, an equiatomic precursor TlSb was prepared (Tl: 99.99 mass % Chempur, additionally refined by re-crystallization from the melt; Sb: 99.99 mass % Chempur). The powdered precursor was ground together with FeSb$_2$ (Fe: 99.99 mass %, Chempur) and Sb powder in stoichiometric ratio within an argon gas-filled glove-box (O$_2$, H$_2$O impurities < 0.1 ppm). This mode of synthesis helps to prevent possible contamination by toxic thallium which must be handled with special care.$^{13}$ Tablets were pressed and sealed into Ta containers which were sealed into quartz tubes and subjected to several heat treatments (425°C for 7 days), regrinding and compacting cycles. The compacted tablets kept their shape during the sintering process. Further efforts to increase the density of the samples were made by spark plasma sintering.$^{14}$ A density of 95 % was achieved. TlFe$_2$Sb$_{12}$ is stable in air and hydrochloric acid.

The samples were characterized using powder X-ray diffraction (XRD) performed on a HUBER G670 imaging plate Guinier camera, equipped with a Ge monochromator and CuK$_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å). The lattice parameters were refined by least-squares fitting of Guinier powder data with LaB$_6$ as internal standard, $a = 4.15692(1)$ Å, by using WinXPOW$^{15}$ and the WinCSD program package.$^{16}$ The crystal structure at room temperature was refined with the WinCSD program based on powder XRD data (CuK$_{\alpha 1}$ radiation) collected on a STOE STADIP-MP diffractometer using a zero-background sample holder. The chemical composition of a single-phase sample (no elemental Sb, FeSb, or FeSb$_2$ impurities could be detected) was deduced by chemical analysis employing the inductively-coupled plasma mass spectroscopy (ICP-MS) method.

Magnetic properties were measured on powders which were treated with concentrated hydrochloric acid to remove impurities of elemental iron.$^2$ Magnetization was determined on a SQUID magnetometer (MPMS XL-7, Quantum Design). zfc (zero-field cooling; measured in heating) and fc runs, and isothermal magnetization curves were measured up to $\mu_0 H_{\text{ext}} = 7$ T. Demagnetization corrections were not applied. Heat capacity was determined by a relaxation method (PPMS Quantum Design). Electrical resistance was measured with ac ($I = 32$ mA, $f = 13$ Hz) on bar-shaped sintered material in a PPMS. Transversal magnetoresistance was determined at constant magnetic fields while sweeping the temperature. Additional magnetoresistance and Hall effect data were obtained from isothermal magnetic
TABLE I: Crystallographic data of TlFe₄Sb₁₂. Space group Im3, lattice parameter at 293 K: \(a = 9.1973(5)\) Å. \(Z = 2\). Calculated mass density: \(\rho = 8.02\) g cm\(^{-3}\). Tl is in 2\(a\) (0, 0, 0); Fe in 8\(c\) (1/4, 1/4, 1/4); Sb in 24\(g\) (0, \(y\), \(z\)). \(2\theta\) range: 10–119.18 degree, linear absorption coefficient: \(\mu = 216.5\) mm\(^{-1}\), mode of refinement: full profile, number of free parameters: 8; \(R_I/R_P:\) 0.047/0.071. \(B_{iso} = 8\pi^2 U_{iso}\) are the isotropic atomic displacement parameters (\(U_{iso}\): mean square amplitude). Occupation (occ.) and \(B_{iso}\) of Tl were refined simultaneously. Some relevant interatomic distances \(d\) are also given, for definitions cf. Ref. 2. Values for the Na compound (neutron diffraction at \(T = 300\) K\(^2\)) are given for comparison.

<table>
<thead>
<tr>
<th>(y)</th>
<th>(z)</th>
<th>occ.(Tl)</th>
<th>(B_{iso}(Tl))</th>
<th>(B_{iso}(Fe))</th>
<th>(B_{iso}(Sb))</th>
<th>(d_{1,2}(Sb\text{--}Sb))</th>
<th>(d(Fe\text{--}Sb))</th>
<th>(d(Tl\text{--}Sb))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TlFe₄Sb₁₂</td>
<td>0.1584(2)</td>
<td>0.3366(2)</td>
<td>0.961(8)</td>
<td>0.76(9)</td>
<td>0.59(11)</td>
<td>0.28(3)</td>
<td>3.006(3), 2.913(3)</td>
<td>2.5751(9)</td>
</tr>
<tr>
<td>NaFe₄Sb₁₂</td>
<td>0.1593(4)</td>
<td>0.3363(4)</td>
<td>1</td>
<td>3.2(4)</td>
<td>0.31(5)</td>
<td>0.51(4)</td>
<td>3.00(1), 2.93(1)</td>
<td>2.57(2)</td>
</tr>
</tbody>
</table>

A standard constant-acceleration equipment was used to collect \(^{57}\)Fe Mössbauer spectra in the temperature range between 4.3 K and 295 K in transmission geometry. For the in-field experiments at 4.2 K and \(\mu_0 H = 13.5\) T (homogeneity 0.1%) calibration was performed by a coupled, simultaneous experiment at room temperature using a \(^{57}\)CoRh source moved with the same driving unit as used for the experiment and an \(\alpha\)-Fe foil. The \(^{57}\)CoRh source for the measurements was mounted on a rod which is coupled to the driving unit and was placed in a field-compensated area inside the cryostat. Source temperatures varied between 5.4 K and 25 K. For the zero-field measurements standard constant-acceleration spectrometers with continuous-flow cryostats were used. Calibration was performed against SNP at room temperature. All center shift (CS) values are given relative to the used sources. The spectra were analyzed by solving the full Hamiltonian taking into account both electrostatic and magnetic hyperfine interactions. Sample thickness was considered using the approximation described in Ref. 17.

To investigate the electronic structure of TlFe₄Sb₁₂ in comparison to the Na and K homologues, a full-potential non-orthogonal local-orbital calculation scheme (FPLO, version 5.00-19)\(^1\) within the local (spin) density approximation (L(S)DA) was used. In the scalar-
relativistic calculations the exchange and correlation potentials of Perdew and Wang were used. As the basis set, Na (2s, 2p, 3s, 3p, 3d), K (3s, 3p, 4s, 4p, 3d), Tl (5s, 5p, 5d, 6s, 6p, 6d), Fe (3s, 3p, 4s, 4p, 3d) and Sb (4s, 4p, 4d, 5s, 5p, 5d) states were employed. The lower-lying states were treated fully relativistically as core states. The Na and K 3d states as well as the Sb 5d and Tl 6d states were taken into account as polarization states to increase the completeness of the basis set. The treatment of the semi-core like states Na (2s, 2p), K (3s, 3p), Tl (5s, 5p, 5d), Fe (3s, 3p) and Sb (4s, 4p, 4d) as valence states was necessary to account for otherwise non-negligible core-core overlaps. The spatial extension of the basis orbitals, controlled by a confining potential \((r/r_0)^4\), was optimized with respect to the total energy. A dense \(k\)-mesh of 1256 points in the irreducible part of the Brillouin zone (27000 in the full zone) was used to ensure accurate density of states and band structure information, especially in the region close to the Fermi level.

FIG. 1: Detail of the X-ray powder diffraction data (a, points) and profile fit (a, line) for TlFe₄Sb₁₂. Ticks label the calculated peaks (b). The line (c) shows the difference \(I_{\text{obs}} - I_{\text{calc}}\).
III. RESULTS

A. Crystal structure

TlFe$_4$Sb$_{12}$ adopts a crystal structure of LaFe$_4$P$_{12}$-type$^{21}$ with a cubic lattice parameter $a = 9.1973(5)$ Å, compared to 9.1767(5) Å and 9.1994(5) Å observed for isostructural NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$, respectively.$^2$ Crystallographic data derived from refinement of powder XRD data of a single-phase sample (see Fig. 1) are summarized in Table I. The Tl cation resides in the voids generated by the tilted FeSb$_6$ octahedra forming the host structure (for a detailed discussion of the skutterudite structure we refer to Ref. 2). From chemical analysis of single-phase samples a composition of Tl$_{0.98(2)}$Fe$_{3.97(2)}$Sb$_{12.04(2)}$ was deduced indicating no significant deviations from nominal stoichiometric composition.

From the refinement of the powder XRD data an occupation of 96.1(8)\% of the Tl 2$a$ site was deduced (in fair agreement with the chemical analysis). Keeping in mind that the occupation factor of the 2$a$ site is strongly correlated with the atomic displacement parameter, and both are influenced by X-ray absorption effects, the degree of filling (for consistency of the following calculations and discussions) was fixed to the value obtained from the chemical analysis ($x = 0.98$). The filling of the icosahedral voids is thus near to complete. This is in contrast to Co-based skutterudite compounds, where a maximum filling of 0.8 is attained in Tl$_{0.8}$Co$_{3}$FeSb$_{12}$ and Tl$_{0.8}$Co$_{4}$Sb$_{11}$Sn at the cost of substituting on either the transition metal or the pnictogen site by one metal atom with one electron less.$^{11}$ The [Fe$_4$Sb$_{12}$] polyanion features four electrons less than [Co$_4$Sb$_{12}$], leading to a full occupation of the icosahedral voids and a charge transfer of one electron from the thallium. Tl however is monovalent in TlFe$_4$Sb$_{12}$ and only its 6$p$ electron is transferred. The ionization energies for formation of Tl$^+$ and K$^+$ cations are low and comparable but, on the other hand, for a Tl$^{3+}$ species it significantly exceeds those values and also those observed for the more electropositive rare-earth metals.$^{22}$ Moreover, the +3 oxidation state would result in a significantly smaller ionic radius, comparable with those observed for the heavy rare-earth ions,$^{23}$ for which no equilibrium MFe$_4$Sb$_{12}$ compounds exist.$^8,^{24}$

Nevertheless, the atomic displacement parameter of Tl is larger than the parameters of Fe and Sb. Such a behavior is observed in all antimony-based filled skutterudites and can be understood in terms of strong vibrations of the cations in the spacious cavities.
of a rather rigid 3-dimensional covalently bonded Fe–Sb framework. Comparing the ratio $B_{\text{iso}}(M)/B_{\text{iso}}(\text{Fe})$ for the Tl and Na compound it is obvious that this ratio increases with decreasing cation size.

**FIG. 2:** (color online) Magnetization $M$/Fe-atom of filled skutterudite TlFe$_4$Sb$_{12}$ versus temperature for different external fields in fc (upper branches) and zfc mode (lower branches). The inset shows $H/M$ for the three highest fields.

**B. Magnetization**

Figure 2 shows the magnetization of TlFe$_4$Sb$_{12}$ in several external fields. In low fields a sharp transition to a ferromagnetic state below $T_C = 80(1)$ K is found, which is smeared out and shifted to higher temperatures by larger fields. The ordering temperature is identical to those of NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ ($T_C = 80(1)$ K, Refs. 1,2). The magnetization at 1.8 K increases strongly with the external field and reaches $\approx 0.50 \mu_B$/Fe-atom at 1 T and 0.62 $\mu_B$/Fe-atom at 7 T. However, the hysteresis is very small and is already closed at fields of order 0.1 T (see Fig. 3), similar to the Na and K homologues.$^{1,2}$ This slow increase of $M$ beyond the technical saturation has been explained by the presence of strong spin fluctuations in the magnetically ordered state.$^2$
The paramagnetic effective moment extracted from a Curie-Weiss fit to $M/H$ at high temperatures yields $1.69 \mu_B/\text{Fe-atom}$ with $\theta_p = +88.3 \text{K}$, i.e. $\theta_p$ is slightly larger than $T_C$. The effective magnetic moment is very similar to that of the Na and K homologues, indicating that this $\mu_{\text{eff}}$ stands for one quarter of the $[\text{Fe}_4\text{Sb}_{12}]$ polyanion. In the case of Na, K, and Tl one electron is transferred from the non-magnetic cation to the $[\text{Fe}_4\text{Sb}_{12}]$ host.\textsuperscript{2,25} Note the large ratio of the paramagnetic effective moment to the ordered moment classifying the compounds as weak itinerant ferromagnets.\textsuperscript{26}

![Diagram of isothermal magnetization loops](image)

**FIG. 3:** (color online) Isothermal magnetization loops $M(H)$ to $\mu_0 H = \pm 1 \text{T}$ for different temperatures for Tl$\text{Fe}_4\text{Sb}_{12}$. $M(1 \text{T})$ decreases with increasing temperature. The inset shows a magnification of the isotherm at $1.8 \text{K}$.

### C. Electrical transport

The electrical resistivity of filled skutterudite compounds strongly depends on the density of the sample.\textsuperscript{7,27} The pure sample of Tl$\text{Fe}_4\text{Sb}_{12}$, whose data are presented here, was not so highly compacted as our other M$\text{Fe}_4\text{Sb}_{12}$ materials ($M = \text{Na, K, Ca, Sr, Ba, etc.}$).\textsuperscript{2} The room temperature resistivity of (as-prepared) Tl$\text{Fe}_4\text{Sb}_{12}$ is about $8.3 \text{m}^\Omega \text{cm}$ and drops to $\rho_0 \approx 0.26 \text{m}^\Omega \text{cm}$ at $1.8 \text{K}$. As a test, a sample of Tl$\text{Fe}_4\text{Sb}_{12}$ was compacted by spark plasma...
sintering (SPS) under similar conditions as other MFe₄Sb₁₂ materials \((p = 0.4 \text{ GPa}, T = 250^\circ \text{C}, \text{duration } 2 \text{ h})\). In this sample \(\rho(300 \text{ K})\) decreased significant to 1.2 m\(\Omega\) cm but \(\rho_0\) was still 0.2 m\(\Omega\) cm. Thereby, it was found from magnetic susceptibility measurements at room temperature that the SPS treatment generated ferromagnetic iron impurities (some 100 ppm). Similar observations were made for other MFe₄Sb₁₂ compounds.²

For pure filled skutterudite samples of different bulk density it has been observed that the resistivity data \(\rho(T)\) can be scaled by a constant factor onto a common curve, i.e. in a porous sample both the residual resistivity \(\rho_0\) and \(\rho(300 \text{ K})\) increase by about the same factor. This remarkable behavior is probably due to a different number of grain boundaries. For that reason we used the as-prepared material also for the magneto-transport measurements. As typically observed for MFe₄Sb₁₂ skutterudites with monovalent M\(^+\) and, especially, with divalent cations M\(^{2+}\), \(\rho(T)\) shows a strong increase with \(T\) below \(\approx 80 \text{ K}\) crossing over to an almost linear increase at higher temperatures.²⁸ Superimposed upon this shoulder in \(\rho(T)\), at \(T_C = 80 \text{ K}\) a sharp change of slope is observed, as clearly seen as a cusp in the derivative \(d\rho/dT\) at 80 K (Fig. 4, inset). As in the Na and K homologues²⁵ the resistivity follows a \(T^2\) dependence to almost 40 K \((\approx T_C/2)\), suggesting a Fermi liquid behavior. A fit of \(\rho(T)\) below 7 K with the expression \(\rho_0 + AT^\alpha\) results in \(\alpha = 2.09\).

The magnetoresistance ratio \((\rho(H) - \rho(0))/\rho(0)\) (MRR) versus temperature is also given in Fig. 4 for three constant fields. There is a negative dip on the MRR at the Curie temperature followed by a large positive value at low temperatures. Qualitatively the same behavior is observed for the ferromagnetic filled skutterudites with M = Na, K,²⁵ but – except for the negative dip at \(T_C\) – also for the paramagnetic compounds with M = Ca, Sr, and Ba.⁵,²⁵

By Hall-effect measurements it has been shown that filled skutterudites with alkali and alkaline-earth cations have a very low uncompensated charge carrier concentration. The Hall resistivity for the SPS-treated TlFe₄Sb₁₂ sample is \(\approx 5 \times 10^{-7} \Omega \text{ cm T}^{-1}\) at 2 K and about half this value at room temperature. This is about a factor of 3 or 4 lower than for KFe₄Sb₁₂ or NaFe₄Sb₁₂, respectively,²⁵ but still a large Hall resistivity, indicating a partial compensation of holes and electrons, in agreement with the electronic structure (see below).
FIG. 4: (color online) Magnetoresistance ratio \((\rho(H) - \rho(0))/\rho(0)\) for TlFe\(_4\)Sb\(_{12}\). The inset shows the resistivity \(\rho(T)\) at zero field and the derivative \(d\rho/dT\).

D. Specific heat

The specific heat capacity of filled skutterudite compounds MFe\(_4\)Sb\(_{12}\) shows two remarkable characteristics.\(^{25}\) Firstly, a large electronic term \(\gamma T\) (\(\gamma \approx 100–200\) mJ mol\(^{-1}\) K\(^{-1}\)) due to a high electronic density of states at \(E_F\) with only a small band mass enhancement both for ferromagnetically ordering and nearly ferromagnetic compounds.\(^{25}\) Secondly, a low-lying vibrational mode due to the vibrations of the filler cation M. A model for the specific heat involving an Einstein mode for the latter contribution has previously been applied to rare-earth\(^5,29\) or thallium\(^11\) ions in skutterudites. In our approach we use only the low-temperature specific heat capacity \((T < \Theta_D/10)\). It can be successfully modeled by an Einstein mode in addition to the usual Debye terms for several filled skutterudite compounds.\(^{25}\) A very similar picture evolves for TlFe\(_4\)Sb\(_{12}\). Figure 5 shows \(c_p(T)\) below 14 K in comparison with other ferromagnetic filled skutterudite compounds.\(^{25}\) Tl is a heavy filler cation and thus, a very low frequency of the vibrational mode can be expected. Indeed, \(c_p(T)\) of TlFe\(_4\)Sb\(_{12}\) is much larger than that of the isostructural Na and K compounds. The fact that this enhancement of \(c_p(T)\) is indeed predominantly due to the Einstein mode can be demonstrated
FIG. 5: (color online) Molar heat capacity of TlFe₄Sb₁₂ (Tl) in a $c_p/T$ vs. $T^2$ representation. For comparison, the data for ferromagnetic NaFe₄Sb₁₂ (Na) and KFe₄Sb₁₂ (K, from Ref. 25) are given. Full lines are fits according to eqn. 1, the dashed lines (from top, for Tl, Na, and KFe₄Sb₁₂, respectively) are the Debye plus Sommerfeld (electronic) contributions.

by an analysis as detailed in a forthcoming publication.²⁵

For TlFe₄Sb₁₂ we can fit the data well to the equation

$$c_p(T) = \gamma T + \beta T^3 + \epsilon E(T/\Theta_E)$$  \hspace{1cm} (1)

where $\epsilon$ is the amplitude of the Einstein term. When setting $\epsilon = 0.98 \times 3R$ ($R$ = molar gas constant) according to the filling factor of Tl in TlFe₄Sb₁₂ the parameters are $\gamma = 127.0(2.5) \text{ mJ mol}^{-1} \text{K}^{-2}$, $\beta = 2.241(38) \text{ mJ mol}^{-1} \text{K}^{-4}$, corresponding to $\Theta_D(0) = 239 \text{ K}$ for 16 atoms, and $\Theta_E = 54.7(3) \text{ K}$. However, the fit shows significant deviations from the data, especially below 5 K, and the resulting $\gamma$ is clearly too large. Including the higher-order term in the Debye approximation, $\delta T^5$, does not improve the fit significantly. If, however, $\epsilon$ is allowed to vary the least squares deviation decreases by a factor of $\approx 50$. The optimum parameters are: $\gamma = 103.5(7) \text{ mJ mol}^{-1} \text{K}^{-2}$, $\beta = 3.181(24) \text{ mJ mol}^{-1} \text{K}^{-4}$. $\epsilon = 16.1(2) \text{ J mol}^{-1} \text{K}^{-1}$, which would correspond to only 0.64 atoms participating in the Einstein term with $\Theta_E = 52.4(1) \text{ K}$. Thus, the degrees of freedom contributing to the Debye
term is slightly larger. Expressed in number of atoms it is 16.98-(\(\epsilon/3R\)) instead of 16. For these 16.34 atoms a Debye temperature \(\Theta_D(0) = 215\,\text{K}\) is obtained.

The resulting \(\epsilon\) is smaller than (filling factor \(\times 3R\)) expected for the full Einstein mode of the cation (a sharp excitation at energy \(\Theta_E/k_B\)). Actually, the analysis of \(c_p(T)\) suggests that only 64\% of the spectral weight of the Tl vibrations are concentrated in the lowest-lying peak of the phonon density of states (PDOS). The above observation of a too small \(\epsilon\) has also been made for the specific heat of some other skutterudites with heavy cations (M = La and Yb).\(^{25}\)

With our fitting model a smaller \(\epsilon\) may indicate a large linewidth of the vibrational mode of Tl. For the related skutterudite Tl\(_{0.8}\)Co\(_3\)FeSb\(_{12}\) however a quite narrow (<0.9 meV) line was observed at 4.9 meV (and assigned to the Tl Einstein mode).\(^{11}\) Thus, we may exclude this possibility. Numerically, contributions or the cations to the PDOS at much higher energies will become absorbed in the Debye term of the fit function for \(c_p(T)\). Since the vibrational properties of the cations depend on the potential inside the icosahedral cage of Sb, the discussion of the cation Einstein term in TlFe\(_4\)Sb\(_{12}\) will be resumed after discussing the electronic structure (section III E). There, also an explanation for the smaller than expected value of \(\epsilon\) will be given. Besides this amplitude \(\epsilon\), the obtained \(\Theta_E\) is very similar to the values observed by Hermann et al.\(^{11}\) via specific heat and inelastic neutron diffraction.

Due to the dominant Fe 3\(d\) and Sb 4\(p\) states at the Fermi level (see below) the value for the Sommerfeld coefficient \(\gamma\) of TlFe\(_4\)Sb\(_{12}\) is of the size observed for other MFe\(_4\)Sb\(_{12}\) with M = Na, K, Ca, Sr, and Ba (100–120 mJ mol\(^{-1}\) K\(^{-2}\)).\(^{25}\)

E. Electronic structure

The calculated non-magnetic total electronic density of states (DOS) for TlFe\(_4\)Sb\(_{12}\) in comparison to KFe\(_4\)Sb\(_{12}\) is plotted in Fig. 6. As a main result, we find that the Tl skutterudite is electronically very similar to the related alkali metal compounds. The valence region above \(-5\) eV, that is predominantly formed by Fe 3\(d\) and Sb 5\(p\) states, shows almost identical width and shape. This leads to the conclusion that Tl in TlFe\(_4\)Sb\(_{12}\) behaves like a monovalent cation. Even the fine structure, i.e. the states close to the Fermi energy \(E_F\), are very similar for the Na, K, and Tl compounds (see inset of Fig. 6). Although the DOS at the Fermi level is slightly smaller in the Tl system than in the Na and K compounds, a
similar magnetic behavior of this series of isostructural compounds can be expected already from the non-magnetic electronic structure.

From the calculated Fermi surface sheets and corresponding band-resolved DOS a strong compensation of hole and electron charge carriers in the TlFe$_4$Sb$_{12}$ system is found, although this compensation is significantly less pronounced compared to the Na and K system. This is in good agreement with the measured Hall data.

Because of the high DOS at $E_F$ and the predominance of Fe 3$d$ states the compound fulfills the Stoner criterion for a magnetic instability. Consequently, a magnetic ground state is expected. In accord with this reasoning, spin polarized LSDA calculations find a ferromagnetic ground state similar to the alkali metal compounds. The spin-polarized DOS is given in Fig. 7. We find a total magnetic moment of 2.9 $\mu_B$ per formula unit. The main contribution is due to the Fe atoms (0.82 $\mu_B$ per atom). Sb ($-0.03 \mu_B$ per atom) and Tl ($-0.06 \mu_B$ per atom) are slightly polarized in the opposite direction. The macroscopic magnetization in low fields, however, is strongly reduced due to spin fluctuations. Like in the alkali metal compounds, the calculated ground state is nearly half metallic, the (static) spin
Fig. 7: (color online) Spin polarized electronic density of states (DOS) for TlFe$_4$Sb$_{12}$. The large Fe and the small Tl contributions are given with areas colored below the curves, the total DOS and the Sb contribution as lines.

Polarization is 96%. This large spin polarization is not expected to persist in real electronic transport, but still a transport spin polarization up to 67% (60%) could be observed for the K (Na) compound and reasons for the reduction of the polarization have been discussed.\textsuperscript{3}

The two main differences in the valence DOS of TlFe$_4$Sb$_{12}$ and the alkali metal compounds are (i) the feature at $-6$ eV originating from the Tl 6$s$ electrons and (ii) the reduced gap size directly above the Fermi level which is related to the $t_{2g}$–$e_g$ crystal field splitting of the Fe 3$d$ states. The narrow width of the band around $-6$ eV indicates a rather localized nature of these Tl states. This localization suggests, in the language of chemical bonding, that they can be considered as lone pair. The low-lying Tl 6$s$ states only weakly hybridize with the 5$s$ states of the surrounding Sb atoms, albeit significantly stronger than the alkali metal ions in NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$. This gives an explanation why the Tl and the alkali metal compounds behave electronically similar. The resulting lattice vibrations (especially those of the cations) of the compounds are however very different.
Recently, Ghosez and Veithen\textsuperscript{30} showed by first-principle calculations for the related model compound TlCo\textsubscript{3}FeSb\textsubscript{12} how this hybridization affects the dynamic properties of Tl in the structure. Good agreement with experimental data\textsuperscript{11} was reported. Thus, contingent on the nature of the cation, a more or less strong hybridization of the cation vibrational modes with modes of the framework can be expected.

Additional peaks in the PDOS or other effects due to hybridization of the vibrations of the cations with the Sb phonons have been observed in some filled skutterudites (notably La\textsubscript{x}Fe\textsubscript{4}Sb\textsubscript{12}),\textsuperscript{29,31–33} by neutron spectroscopy. The most clear-cut result was obtained for Eu\textsubscript{x}Fe\textsubscript{4}Sb\textsubscript{12}, where, by nuclear inelastic scattering, the partial PDOS for Eu atoms was determined.\textsuperscript{34} For the Eu\textsuperscript{2+} cation three distinct peaks were observed at 7.3(1), 12.0(4), and 17.8(5) meV with different spectral weights. This splitting of the cation mode is consistent with \textit{ab initio} PDOS calculations.\textsuperscript{30,33,35} The peaks at higher energy are found – as expected – in the PDOS region of the Sb vibrations. The relative spectral weight of the lowest-lying peak was only 68\% and a similar distribution of cation PDOS can be expected for other heavy cations in skutterudites. Actually, this value for Eu\textsuperscript{2+} ions compares favorably with the value observed in our specific heat data for Tl\textsuperscript{1+} ions. For further discussions of the topic on a wider range of cations see Refs. 28 and 32.

F. Mössbauer spectroscopy

\textsuperscript{57}Fe Mössbauer spectroscopy has been applied as a local probe for the magnetic interactions in TlFe\textsubscript{4}Sb\textsubscript{12} (Fig. 8). The results can be compared with our previous measurements on NaFe\textsubscript{4}Sb\textsubscript{12}.\textsuperscript{2} Due to the asymmetry in the spectra of the Tl compound (best visible in the in-field measurements of Fig. 8c) a superposition was necessary of at least two subspectra with area ratio around 80:20 and line widths of approximately 0.24 mm s\textsuperscript{-1} to obtain a reasonable fit. In zero external field above \(T_C = 80\) K only quadrupole split spectra were recorded (e.g., Fig. 8a). The values for the quadrupole splitting decrease slightly with temperature (Fig. 9).

Below 80 K magnetic hyperfine splitting appears. At 4.2 K and external fields \(\mu_0 H_{\text{ext}} \leq 4\) T complete alignment of external and internal fields can be assumed because of the vanishing of the \(\Delta m = 0\) transitions. From the difference of external fields and the measured hyperfine fields the induced fields, \(\mu_0 H_{\text{ind}}\), were deduced for the two subspectra. \(\mu_0 H_{\text{ind}}\) of
FIG. 8: (color online) $^{57}$Fe Mössbauer spectra recorded in transmission geometry at zero (a, b) and $\mu_0 H = 13.5$ T (c) external field at various temperatures. The full lines are fits to the data assuming a superposition of two subspectra indicated by dashed (80%) and dotted lines (20% of the total area).

0.7 T (majority component) and 1.8 T (minority component) were obtained. These values for the subspectra are independent of $\mu_0 H_{\text{ext}}$ as expected for a ferromagnetically ordered compound. In a previous study on NaFe$_4$Sb$_{12}$ in zero external field $\mu_0 H_{\text{ind}} = 1.64$ T was found.$^2$
FIG. 9: (color online) Temperature dependence of the quadrupole splitting $eQV_{zz}/4$ for different Fe atom sites. Full circles (squares): Fe atoms allocated to the spectrum with the large (small) intensity. The lines are guides to the eyes. Values reported by Long et al.\textsuperscript{10} for Tl-deficient Co-containing skutterudites are shown for comparison. Open circles (squares): Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl\textsubscript{0.8}Co\textsubscript{3}FeSb\textsubscript{12}. Open diamonds (stars): Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl\textsubscript{0.5}Co\textsubscript{3.5}Fe\textsubscript{0.5}Sb\textsubscript{12}. Similarly small $\mu_0H_{\text{ind}}$ values, however, with opposite sign were obtained for Eu\textsubscript{0.88}Fe\textsubscript{4}Sb\textsubscript{12}.\textsuperscript{36}

From the temperature dependence of the center shift (Fig. 10) Debye temperatures for the two sites were determined (with the assumption of a temperature-independent isomer shift) by expressing the second order Doppler shift, $SOD$, via

$$SOD(T) = \frac{3k_B T}{2mc} \left[ \frac{3\Theta_D}{8T} + 3 \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right],$$

with $x = \hbar \omega/k_BT$, $m$ the mass of the $^{57}$Fe nucleus, $k_B$ the Boltzmann constant, and $c$ the velocity of light.

Whereas for the component with the larger spectral area a value of $\Theta_D = (555\pm45)$ K results, $\Theta_D = (350\pm40)$ K was found for the minority Fe site. Debye temperatures obtained from the temperature dependence of the center shift usually differ from those values extracted from specific heat data, because the former is connected with the local vibrations
FIG. 10: (color online) Temperature dependence of the center shift (CS). Full circles (squares): Fe atoms allocated to the spectrum with the large (small) intensity. The lines are fits according to the Debye model. Values reported by Long et al.\textsuperscript{10} for Tl-deficient Co-containing skutterudites are shown for comparison. Open circles (squares): Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl\textsubscript{0.8}Co\textsubscript{3}FeSb\textsubscript{12}. Open diamonds (stars): Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl\textsubscript{0.5}Co\textsubscript{3.5}Fe\textsubscript{0.5}Sb\textsubscript{12}.

of a specific atom (\textsuperscript{57}Fe) while the latter represents an average for the whole lattice (here, the host structure [Fe\textsubscript{4}Sb\textsubscript{12}]). Smaller Debye temperatures are also obtained from EXAFS measurements on CeFe\textsubscript{4}Sb\textsubscript{12} (\(\Theta_D = 390\text{ K}^{37}\)) while from Mössbauer investigations a value of 450 K is derived.\textsuperscript{38} The difference correlates well with the results obtained from our calculations of the binding energies which indicate a much stiffer Fe-Sb binding compared to the Sb-Sb bond.\textsuperscript{2}

Although crystallographically only one Fe site is present in the structure, at least two subspectra are necessary to analyze the obtained Mössbauer spectra in a consistent way. The spectrum with lower intensity is not due to binary Fe-Sb impurities since the reported hyperfine parameters are quite different.\textsuperscript{39} Two subspectra were also obtained for other incompletely filled skutterudites Pr\textsubscript{0.73}Fe\textsubscript{4}Sb\textsubscript{12} and Eu\textsubscript{0.88}Fe\textsubscript{4}Sb\textsubscript{12};\textsuperscript{36,40} where the number of voids on the cation sites can be correlated with the spectral area ratio of the Mössbauer analyses. This agreement led to the assumption that the \textsuperscript{57}Fe probe atom is either surrounded by two
(complete filling), one, or zero (partly filling) M cations in the next-nearest neighbor shell. Due to these different surroundings, different spectra will be obtained. Since for TiFe\textsubscript{4}Sb\textsubscript{12}, the occupation is high (98(2)\%), the probability (in case of a statistical distribution) of two neighboring voids is small (e.g. for the occupation number of 0.98 one gets a probability of 0.960, 0.039, and 0.000 for 2, 1, and 0 Tl atoms, respectively). A similar scenario was suggested for the strongly sub-stoichiometric Co-based Tl skutterudites Tl\textsubscript{0.8}Co\textsubscript{3}FeSb\textsubscript{12} and Tl\textsubscript{0.5}Co\textsubscript{3.5}Fe\textsubscript{0.5}Sb\textsubscript{12} by Long et al.\textsuperscript{10}, but it was called into question, because of the deviation of the observed area ratio of the subspectra from the one expected by taking into account a binomial distribution.

From the area ratio of the present investigation a void concentration of at least 10\% follows. Results of chemical and structural analyses point, however, to a filling of at least 96\%. This discrepancy makes an interpretation of the two different Fe sites in terms of voids in the surrounding Tl shells of the Fe species difficult. In contrast to semiconducting TlCo\textsubscript{3}FeSb\textsubscript{12} (Ref. 30) there exists at present no experimental clue or a theoretical indication for a difference in the charge density at the Fe site in metallic skutterudites.

IV. CONCLUSIONS

A new filled skutterudite with [Fe\textsubscript{4}Sb\textsubscript{12}] host and monovalent thallium cation has been synthesized and chemically and structurally characterized. The magnetic, thermal and \textsuperscript{57}Fe Mössbauer effect measurements all show that TiFe\textsubscript{4}Sb\textsubscript{12} is a weak itinerant electron ferromagnet with \(T_C \approx 80\) K, very similar to the isostructural skutterudites with the filler cations Na\textsuperscript{+} and K\textsuperscript{+}. Electronic band structure calculations confirm the itinerant ferromagnetism and predict a half-metallic behavior with a high spin polarization. This should result in a large conduction electron spin polarization in TiFe\textsubscript{4}Sb\textsubscript{12}, as recently demonstrated for the Na and K analogs. Specific heat has detected a low-lying Einstein mode (\(\Theta_E = 53\) K) which is related to the vibrations of the heavy Tl cation in the icosahedral Sb cage. From the specific heat data indications are found and discussed, that the cation (Tl) vibrations have a significant hybridization with the host atoms (Sb). As a consequence, the Einstein mode in low-temperature specific heat comprises only a part of cation vibrations. \textsuperscript{57}Fe Mössbauer spectroscopy shows a small hyperfine splitting below \(T_C = 80\) K and revealed a second weak subspectrum, whose origin is not yet clear. Conclusively we have established a third Fe-
Sb based itinerant ferromagnet in which the magnetic moment solely results from band magnetism of Fe-Sb states at the Fermi level.

ACKNOWLEDGMENTS

H.R. acknowledges the Deutsche Forschungsgemeinschaft (Emmy-Noether-Programm) and J.A.M. the Alexander-von-Humboldt Stiftung for financial support. This work has been partially performed within the European network of excellence “Complex Metallic Alloys (CMA)”. We thank G. Auffermann for the chemical analysis work and are indebted to M. Baitinger for providing us with rectified thallium metal.
* Electronic address: jasper@cpfs.mpg.de

† Permanent address: II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln.


27 The electrical resistivity of polycrystalline samples strongly depends on their porosity which can be effectively reduced by SPS treatment (see, e.g., Ref. [41]).
28 W. Schnelle et al., unpublished.


