

TlFe₄Sb₁₂: Weak itinerant ferromagnetic analogue to alkali-metal iron-antimony skutterudites

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Structural, thermal, electronic, and electrical transport properties as well as high-field ⁵⁷Fe Mössbauer investigations are reported for thallium iron antimonide TlFe₄Sb₁₂, in which thallium attains the formal charge of +1. Similar to the isostructural NaFe₄Sb₁₂ and KFe₄Sb₁₂ 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 ground state 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 [Fe₄Sb₁₂] 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 ⁵⁷Fe Mössbauer spectroscopy confirms the magnetic character.

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I. INTRODUCTION

Recently, we have shown by experimental and theoretical investigations that filled skutterudites $M\text{Fe}_4\text{Sb}_{12}$ with the alkali metals sodium and potassium as M component (“filler”) represent a distinct class of itinerant weak ferromagnetic half-metals.^{1–3} In these compounds, the alkali metals donate one electron to the iron-antimony [Fe₄Sb₁₂] framework (“host”), which gives rise to the stabilization of a highly spin-polarized ferromagnetic ground state below $T_C \approx 80$ K.³ 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} with the exception of Eu_{*x*}Fe₄Sb₁₂, where a ferrimagnetic spin structure of the Fe and Eu²⁺ sublattice is observed.^{8,9}

In their systematic studies of thermoelectric properties of filled skutterudites based on CoSb₃, Sales *et al.*¹⁰ synthesized and characterized the compounds Tl_{*x*}Co₄Sb_{12–*y*}Sn_{*y*} and Tl_{*x*}Co_{4–*y*}Fe_{*y*}Sb₁₂ with Tl contents up to $x=0.8$.^{10–13} Mainly, the thermal and electrical transport properties as well as the phonon spectra of these materials 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 and as a peak in inelastic neutron scattering experiments.^{11,13}

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,¹⁴ prompted us to synthesize the compound TlFe₄Sb₁₂, which represents a skutterudite completely based on iron as a 3*d* metal. In contrast to Co-based skutterudites,^{11–13} in TlFe₄Sb₁₂ 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 [Fe₄Sb₁₂] polyanion.

In this work, we show the results of magnetization, electrical resistivity, magnetoresistance, Hall effect, heat capacity, and high-field ⁵⁷Fe Mössbauer measurements as well as detailed electronic structure calculations. TlFe₄Sb₁₂ 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. EXPERIMENT

The synthesis of TlFe₄Sb₁₂ 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 recrystallization from the melt; Sb: 99.99 mass% Chempur). The powdered precursor was ground together with FeSb₂ (Fe: 99.99 mass%, Chempur) and Sb powder in stoichiometric ratio within an argon gas-filled glovebox (O₂, H₂O impurities <1 ppm). This mode of synthesis helps to prevent possible contamination by toxic thallium, which must be handled with special care.¹⁵ 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.¹⁶ A density of 95% was achieved. No crystals suitable for single crystal x-ray diffraction could be obtained. TlFe₄Sb₁₂ 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 Cu $K\alpha_1$ radiation ($\lambda=1.54056$ Å). The lattice parameters were refined by least-squares fitting of Guinier powder data

with LaB_6 as internal standard, $a=4.156\,92(1)$ Å, by using WINXPOW (Ref. 17) and WINCSD (Ref. 18) program packages. The crystal structure at room temperature was refined with the WINCSD program based on powder XRD data ($\text{Cu } K\alpha_1$ 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 optical emission spectroscopy method.

Magnetization was determined on a superconducting quantum interference device magnetometer (MPMS XL-7, Quantum Design). Zero-field cooling (ZFC, measured in heating) and field cooling (FC) runs, and isothermal magnetization curves were measured up to $\mu_0 H_{\text{ext}}=7$ T. Demagnetization corrections were not applied. Magnetic properties were measured on powders which were treated with concentrated hydrochloric acid to reduce the concentration of an elemental iron impurity.² Susceptibility data in high fields, however, indicated that some residual ferromagnetic impurities ($T_C \gg 400$ K) were still present in the sample. Thus, an extrapolation of $\chi(T)$ vs $1/H \rightarrow 0$ was applied (Honda-Owen method^{2,19}) to obtain the susceptibility of the compound.

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 field sweeps ($\mu_0 H_{\text{ext}}=0$ T \rightarrow 9 T \rightarrow 0 T).

A standard constant-acceleration equipment was used to collect ^{57}Fe Mössbauer spectra in the temperature range between 43 and 295 K in transmission geometry. Calibration was performed against sodium nitroprusside (SNP) at room temperature. 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 $^{57}\text{CoRh}$ source moved with the same driving unit as used for the experiment and an $\alpha\text{-Fe}$ foil. The $^{57}\text{CoRh}$ 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 and 25 K. 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. 20.

To investigate the electronic structure of $\text{TlFe}_4\text{Sb}_{12}$ in comparison to the Na and K homologues, a full-potential nonorthogonal local-orbital calculation scheme (FPLO,²¹ version 5.00-19) within the local (spin) density approximation (L(S)DA) was used. In the scalar-relativistic calculations, the exchange and correlation potentials of Perdew and Wang²² 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

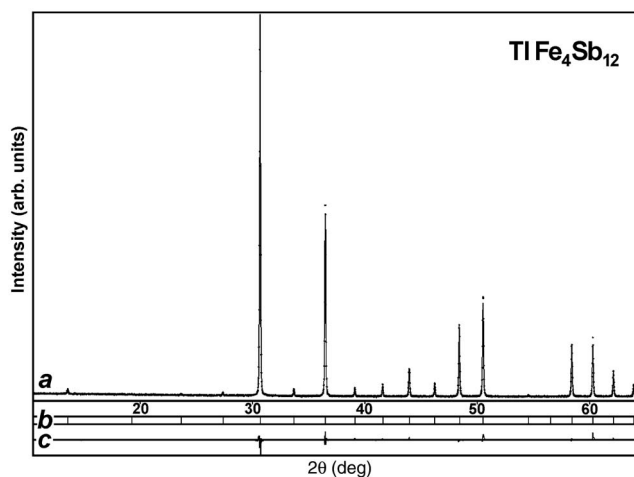


FIG. 1. X-ray powder diffraction data (*a*, measured points) and calculated profile (*a*, line) for $\text{TlFe}_4\text{Sb}_{12}$. Ticks label the calculated peak positions (*b*). The line (*c*) shows the difference $I_{\text{obs.}} - I_{\text{calc.}}$.

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.²³ A dense k mesh of 1256 points in the irreducible part of the Brillouin zone (27 000 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.

III. RESULTS

A. Crystal structure

$\text{TlFe}_4\text{Sb}_{12}$ adopts a crystal structure of $\text{LaFe}_4\text{P}_{12}$ type²⁴ with a cubic lattice parameter $a=9.1973(5)$ Å, compared to $9.1767(5)$ and $9.1994(5)$ Å observed for isostructural $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$, respectively.² Crystallographic data derived from powder XRD experiments 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 $\text{Tl}_{0.98(2)}\text{Fe}_{3.97(2)}\text{Sb}_{12.04(2)}$ was deduced, indicating no significant deviations from nominal stoichiometric composition.

In the refinement of the powder XRD data, the occupation and the atomic displacement parameter of the atom on the $2a$ site (Tl) were refined simultaneously. An occupation of 96.1(8)% of the $2a$ site with Tl was deduced. It has to be kept in mind that the occupation factor of the $2a$ site is strongly correlated with the atomic displacement parameter, and both are influenced by x-ray absorption effects. Since the occupation factor is in fair agreement with the chemical analysis, the degree of filling (for consistency of the follow-

TABLE I. Crystallographic data of TlFe₄Sb₁₂. Space group $Im\bar{3}$, lattice parameter at 293 K: $a=9.1973(5)$ Å. $Z=2$. Calculated mass density: $\rho=8.02$ g cm⁻³. Tl is in $2a$ (0, 0, 0), Fe in $8c$ (1/4, 1/4, 1/4), and Sb in $24g$ (0, y , z). 2θ range: 10° – 119.18° , linear absorption coefficient: $\mu=216.5$ mm⁻¹, mode of refinement: full profile, number of free parameters: 8; R_1/R_p : 0.047/0.071. $B_{\text{iso}}=8\pi^2 \cdot U_{\text{iso}}$ are the isotropic atomic displacement parameters (U_{iso} : square amplitude). Occupation with $M=\text{Tl}$ (Occ.) and B_{iso} of the $2a$ position were refined simultaneously. Some relevant interatomic distances d are also given (for definitions, see Ref. 2). Values for the Na compound (neutron diffraction at $T=300$ K) (Ref. 2) are given for comparison $a=9.1759(8)$ Å.

	y	z	Occ.($2a$)	$B_{\text{iso}}(M)$ (Å ²)	$B_{\text{iso}}(\text{Fe})$ (Å ²)	$B_{\text{iso}}(\text{Sb})$ (Å ²)	$d_1, d_2(\text{Sb-Sb})$ (Å)	$d(\text{Fe-Sb})$ (Å)	$d(M\text{-Sb})$ (Å)
TlFe ₄ Sb ₁₂	0.1584(2)	0.3366(2)	0.961(8)	0.76(9)	0.59(11)	0.28(3)	3.006(3), 2.913(3)	2.5751(9)	3.421(2)
NaFe ₄ Sb ₁₂	0.1593(4)	0.3363(4)	1	3.2(4)	0.31(5)	0.51(4)	3.00(1), 2.93(1)	2.57(2)	3.415(4)

ing calculations and discussions) was fixed to the value obtained from the chemical analysis (viz. $x=0.98$). The fair agreement of the occupation values from both methods also confirms the trustability of the other parameters refined from the XRD data. Since no crystals are available for a more thorough study of the structural parameters, more accurate values, e.g., for the atomic displacement parameters, could not be obtained until now.

The filling of the icosahedral voids with Tl is, thus, nearly complete. This is in contrast to Co-based skutterudite compounds, where a maximum filling of 0.8 is attained in Tl_{0.8}Co₃FeSb₁₂ and Tl_{0.8}Co₄Sb₁₁Sn at the cost of substituting on either the transition metal or the pnictogen site by one atom with one electron less.¹³ The [Fe₄Sb₁₂] polyanion features four electrons less than [Co₄Sb₁₂], leading to a full occupation of the icosahedral voids and a charge transfer of one electron from the thallium. Tl, however, is monovalent in TlFe₄Sb₁₂ and only its $6p$ electron is transferred. The ionization energies for formation of Tl⁺ and K⁺ cations are low and comparable, but, on the other hand, for a Tl³⁺ species it significantly exceeds those values and also those observed for the more electropositive rare-earth metals.²⁵ Moreover, the +3 oxidation state would result in a significantly smaller ionic radius, comparable with those observed for the heavy rare-earth ions,²⁶ for which no equilibrium MFe₄Sb₁₂ compounds exist.^{10,27}

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 three-dimensional covalently bonded Fe-Sb framework.² 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 size and decreasing atomic mass of the cation. The fact that $B_{\text{iso}}(\text{Fe}) > B_{\text{iso}}(\text{Sb})$ in TlFe₄Sb₁₂ is in accord with the atomic mass ratio, suggesting that, predominantly, the thermal motion determines the atomic displacement.

B. Magnetization

Figure 2 shows the magnetization of TlFe₄Sb₁₂ 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 NaFe₄Sb₁₂ and

KFe₄Sb₁₂ [$T_C=80(1)$ K, Refs. 1 and 2]. The magnetization at 1.8 K increases strongly with the external field and reaches $\approx 0.50\mu_B/\text{Fe-atom}$ at 1 T and $0.62\mu_B/\text{Fe-atom}$ 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 For FC curves, the magnetization increases with decreasing temperature in the usual fashion; however, for ZFC curves, in some samples a steplike increase of the magnetization with increasing temperature (as for the sample presented in Fig. 2) at around 30 K is observed. This effect is probably correlated with a peak seen in the ac susceptibility of some NaFe₄Sb₁₂ samples,¹ which is presumably due to domain or relaxation effects.

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 $\theta_p=+88.3$ K, i.e., θ_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 μ_{eff} stands for one-quarter of the [Fe₄Sb₁₂] polyanion. In the case of Na, K, and Tl, one electron is transferred from the non-magnetic cation to the [Fe₄Sb₁₂] host.^{2,28} Note the large ratio of the paramagnetic effective moment to the ordered mo-

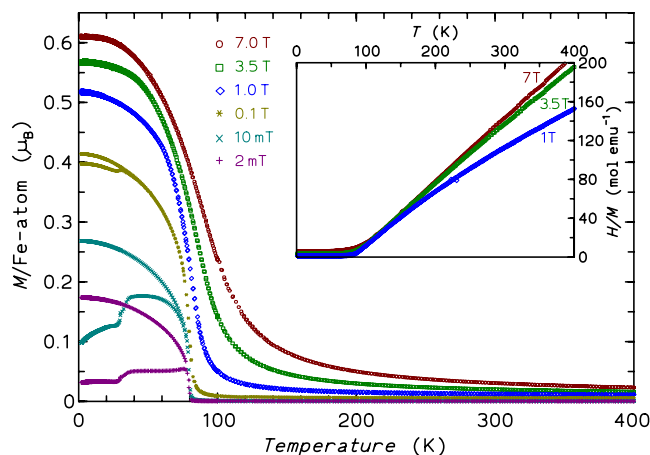


FIG. 2. (Color online) Magnetization $M/\text{Fe-atom}$ of filled skutterudite TlFe₄Sb₁₂ versus temperature for different external fields in FC (upper branches) and ZFC mode (lower branches). The inset shows H/M for the three highest fields.

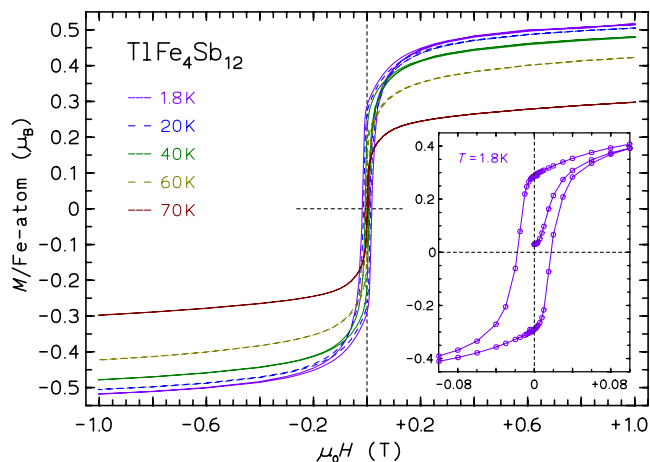


FIG. 3. (Color online) Isothermal magnetization loops $M(H)$ to $\mu_0 H = \pm 1$ T for different temperatures for $\text{TlFe}_4\text{Sb}_{12}$. $M(1 \text{ T})$ decreases with increasing temperature. The inset shows a magnification of the isotherm at 1.8 K.

ment, classifying the compounds as weak itinerant ferromagnets.²⁹

C. Electrical transport

The electrical resistivity of filled skutterudite compounds strongly depends on the density of the sample.^{7,30} The pure sample of $\text{TlFe}_4\text{Sb}_{12}$, whose data are presented here, was not so highly compacted as our other $M\text{Fe}_4\text{Sb}_{12}$ materials ($M = \text{Na, K, Ca, Sr, Ba, etc.}$).² The room temperature resistivity of (as-prepared) $\text{TlFe}_4\text{Sb}_{12}$ is about 8.3 m Ω cm and drops to $\rho_0 \approx 0.26$ m Ω cm at 1.8 K. As a test, a sample of $\text{TlFe}_4\text{Sb}_{12}$ was compacted by spark plasma sintering (SPS) under similar conditions as other $M\text{Fe}_4\text{Sb}_{12}$ materials ($p = 0.4$ GPa, $T = 250$ °C, and duration of 2 h). In this sample, $\rho(300 \text{ K})$ decreased significantly to 1.2 m Ω cm, but ρ_0 was still 0.2 m Ω 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 $M\text{Fe}_4\text{Sb}_{12}$ compounds.²

For pure filled skutterudite samples of different bulk densities, 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 ρ_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 magnetotransport measurements. As typically observed for $M\text{Fe}_4\text{Sb}_{12}$ skutterudites with monovalent M^+ and, especially, with divalent cations M^{2+} , $\rho(T)$ shows a strong increase with T below ≈ 80 K, crossing over to an almost linear increase at higher temperatures.²⁸ Superimposed upon this shoulder in $\rho(T)$, at $T_C = 80$ 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 homologues,²⁸ the resistivity follows a T^2 dependence to almost 40 K ($\approx T_C/2$), suggesting a Fermi liquid behavior. A

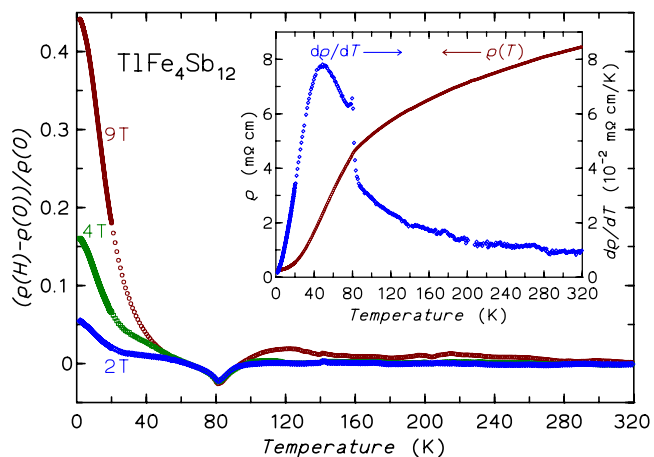


FIG. 4. (Color online) Magnetoresistance ratio $[\rho(H) - \rho(0)]/\rho(0)$ for $\text{TlFe}_4\text{Sb}_{12}$. The inset shows the resistivity $\rho(T)$ at zero field and the derivative $d\rho/dT$.

fit of $\rho(T)$ below 7 K with the expression $\rho_0 + AT^\alpha$ results in $\alpha = 2.09$.

The magnetoresistance ratio MRR $[\rho(H) - \rho(0)]/\rho(0)$ 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 $M = \text{Na}$ and K ²⁸ but—except for the negative dip at T_C —also for the paramagnetic compounds with $M = \text{Ca, Sr, and Ba}$.^{5,28} 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 $\text{TlFe}_4\text{Sb}_{12}$ 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 $\text{KFe}_4\text{Sb}_{12}$ or $\text{NaFe}_4\text{Sb}_{12}$, respectively,²⁸ but still a large Hall resistivity, indicating a partial compensation of holes and electrons, in agreement with the electronic structure (see below).

D. Specific heat

The specific heat of filled skutterudite compounds $M\text{Fe}_4\text{Sb}_{12}$ shows two remarkable characteristics.²⁸ First, a large electronic term γT ($\gamma \approx 100\text{--}200 \text{ mJ mol}^{-1} \text{ K}^{-1}$) due to a high electronic density of states at E_F with only a small band mass enhancement both for ferromagnetically ordered and nearly ferromagnetic compounds.²⁸ Second, 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^{5,31} or thallium¹³ ions in skutterudites. In our approach, we use only the low-temperature specific heat ($T < \Theta_D/10$). It can be successfully modeled by an Einstein mode in addition to the usual Debye terms for several filled skutterudite compounds.²⁸ A very similar picture evolves for $\text{TlFe}_4\text{Sb}_{12}$. Figure 5 shows $c_p(T)$ below 14 K in comparison with other ferromagnetic filled skutterudite compounds.²⁸ Tl is a heavy filler cation and, thus, a very low frequency of the

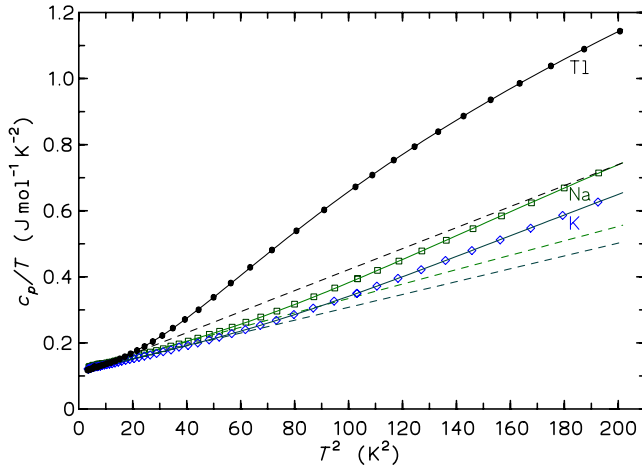


FIG. 5. (Color online) Specific heat of TlFe₄Sb₁₂ (Tl) in a c_p/T vs T^2 representation. For comparison, the data for ferromagnetic NaFe₄Sb₁₂ (Na) and KFe₄Sb₁₂ (K, from Ref. 28) are given. Full lines are fits according to Eq. (1); the dashed lines (from top, for Tl, Na, and KFe₄Sb₁₂, respectively) are the Debye plus Sommerfeld (electronic) contributions.

vibrational mode can be expected. Indeed, $c_p(T)$ of TlFe₄Sb₁₂ 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 by an analysis as detailed in a forthcoming publication.²⁸

For TlFe₄Sb₁₂, we can fit the data well to the equation

$$c_p(T) = \gamma T + \beta T^3 + \epsilon E(T/\Theta_E), \quad (1)$$

where ϵ 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 $\gamma = 127.0(2.5)$ mJ mol⁻¹ K⁻² and $\beta = 2.241(38)$ mJ mol⁻¹ K⁻⁴, corresponding to $\Theta_D(0) = 239$ K for 16 atoms, and $\Theta_E = 54.7(3)$ K. However, the fit shows significant deviations from the data, especially below 5 K, and the resulting γ is clearly too large. Including the higher-order term in the Debye approximation, δT^5 , does not improve the fit significantly. If, however, ϵ is allowed to vary, the least-squares deviation decreases by a factor of ≈ 50 . The optimum parameters are $\gamma = 103.5(7)$ mJ mol⁻¹ K⁻² and $\beta = 3.181(24)$ mJ mol⁻¹ K⁻⁴. $\epsilon = 16.1(2)$ J mol⁻¹ K⁻¹, which would correspond to only 0.64 atoms participating in the Einstein term with $\Theta_E = 52.4(1)$ K. Thus, the number of 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 $\Theta_D(0) = 215$ K is obtained.

The resulting ϵ is smaller than (filling factor $\times 3R$) expected for the full Einstein mode of the cation (a sharp excitation at energy Θ_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 ϵ has also been made for the specific heat of some

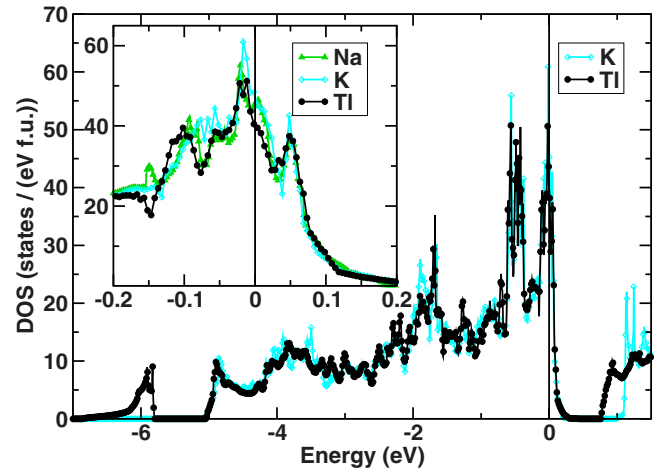


FIG. 6. (Color online) Total paramagnetic electronic density of states (DOS) for TlFe₄Sb₁₂ (Tl, black symbols and line) and KFe₄Sb₁₂ (K, cyan symbols and line). E_F is at zero energy. The inset shows a magnification around E_F and shows also the DOS of NaFe₄Sb₁₂ (Na).

other skutterudites with heavy cations ($M = \text{La}$ and Yb).²⁸

With our fitting model, a smaller ϵ may be partially caused by a large linewidth of the vibrational mode of Tl. For the related skutterudite Tl_{0.8}Co₃FeSb₁₂, however, a quite narrow (< 0.9 meV) line was observed at 4.9 meV (and assigned to the Tl Einstein mode).¹³ Thus, we consider this effect as not that important. In our fitting model, contributions of 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 TlFe₄Sb₁₂ will be resumed after discussing the electronic structure (Sec. III E). There, also an explanation for the smaller than expected value of ϵ will be given. Besides this amplitude ϵ , the obtained Θ_E is very similar to the values observed by Hermann *et al.*¹³ via specific heat and inelastic neutron scattering.

Due to the dominant Fe 3d and Sb 4p states at the Fermi level (see below), the value for the Sommerfeld coefficient γ of TlFe₄Sb₁₂ is of the size observed for other $M\text{Fe}_4\text{Sb}_{12}$, with $M = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{and Ba}$ (100–120 mJ mol⁻¹ K⁻²).²⁸

E. Electronic structure

The calculated nonmagnetic total electronic density of states (DOS) for TlFe₄Sb₁₂ in comparison to KFe₄Sb₁₂ 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 region above -5 eV, which is predominantly formed by Fe 3d and Sb 5p states, shows almost identical width and shape. This leads to the conclusion that Tl in TlFe₄Sb₁₂ 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 TlFe₄Sb₁₂ than in the Na and K compounds, a similar magnetic behavior of this series of isostructural com-

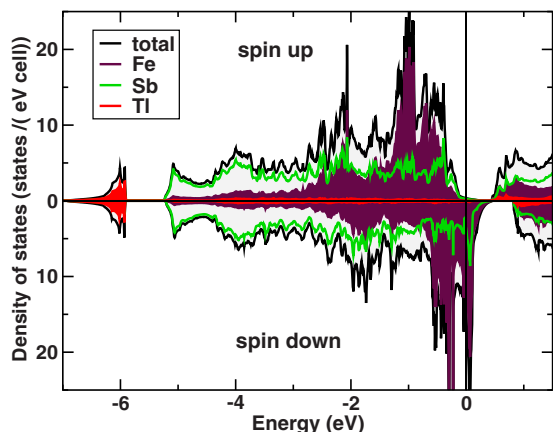


FIG. 7. (Color online) Spin-polarized electronic DOS for $\text{TlFe}_4\text{Sb}_{12}$. The large Fe and the small Tl contributions are given with areas colored below the curves, the total DOS and the Sb contribution as lines.

pounds can be expected already from the nonmagnetic electronic structure.

From the calculated Fermi surface sheets and corresponding band-resolved DOS, a strong compensation of hole and electron charge carriers in the $\text{TlFe}_4\text{Sb}_{12}$ system is found, although this compensation is significantly less pronounced compared to the Na and K systems.²⁸ This is in good agreement with the measured Hall data.

Because of the high DOS at E_F and the predominance of Fe 3d 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.² 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,³ the calculated ground state is nearly half-metallic, the (static) spin 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.³

The two main differences in the valence DOS of $\text{TlFe}_4\text{Sb}_{12}$ and the alkali-metal compounds are (i) the feature at -6 eV originating from the Tl 6s 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 3d 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 a lone pair. The low-lying Tl 6s states only weakly hybridize with the 5s states of the surrounding Sb atoms, albeit significantly stronger than the alkali-metal ions in $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$. This gives an explanation for

the charge transfer and 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 Veithen³² showed, by first-principles calculations for the related model compound $\text{TlCo}_3\text{FeSb}_{12}$, how this hybridization affects the dynamic properties of Tl in the structure. Good agreement with experimental data¹³ 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 $\text{La}_x\text{Fe}_4\text{Sb}_{12}$, Refs. 31 and 33–35) by neutron spectroscopy. The most clear-cut result was obtained for $\text{Eu}_x\text{Fe}_4\text{Sb}_{12}$, where, by nuclear inelastic scattering, the partial PDOS for Eu atoms was determined.³⁶ For the Eu^{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 *ab initio* PDOS calculations.^{32,33,37} The peaks at higher energy are found, as expected, in the PDOS region of the Sb vibrations. Recently, the PDOS for Sb atoms could also be determined by nuclear inelastic scattering for a filled ($\text{Eu}_x\text{Fe}_4\text{Sb}_{12}$) and an unfilled skutterudite (CoSb_3).³⁸ A small peak in the difference of the Sb-PDOS of both compounds is evidence for a weak coupling of the host lattice vibrations with those of the cation. This weak coupling is currently discussed in connection with the lower thermal conductivity of filled cage compounds compared to their unfilled variants.

For $\text{Eu}_x\text{Fe}_4\text{Sb}_{12}$, the relative spectral weight of the lowest-lying peak in the Eu-PDOS was only 68%,³⁶ and a similar distribution of cation PDOS can be expected for other heavy cations in skutterudites. Actually, this value for Eu^{2+} ions compares favorably with the value observed in our specific heat data for Tl^{1+} ions. For further discussions of the topic on a wider range of cations, see Refs. 28 and 39.

F. Mössbauer spectroscopy

^{57}Fe Mössbauer spectroscopy has been applied as a local probe for the magnetic interactions in $\text{TlFe}_4\text{Sb}_{12}$ (Fig. 8). The results can be compared with our previous measurements on $\text{NaFe}_4\text{Sb}_{12}$.² Due to the asymmetry in the spectra of the Tl compound [best visible in the in-field measurements of Fig. 8(c)], a superposition was necessary of at least two subspectra with area ratio around 80:20 and linewidths of approximately 0.24 mm s^{-1} to obtain a reasonable fit. In zero external field above $T_C=80$ K, only quadrupole split spectra were recorded [e.g., Fig. 8(a)]. 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 $\mu_0 H_{\text{ext}} \geq 4$ 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. $\mu_0 H_{\text{ind}}$

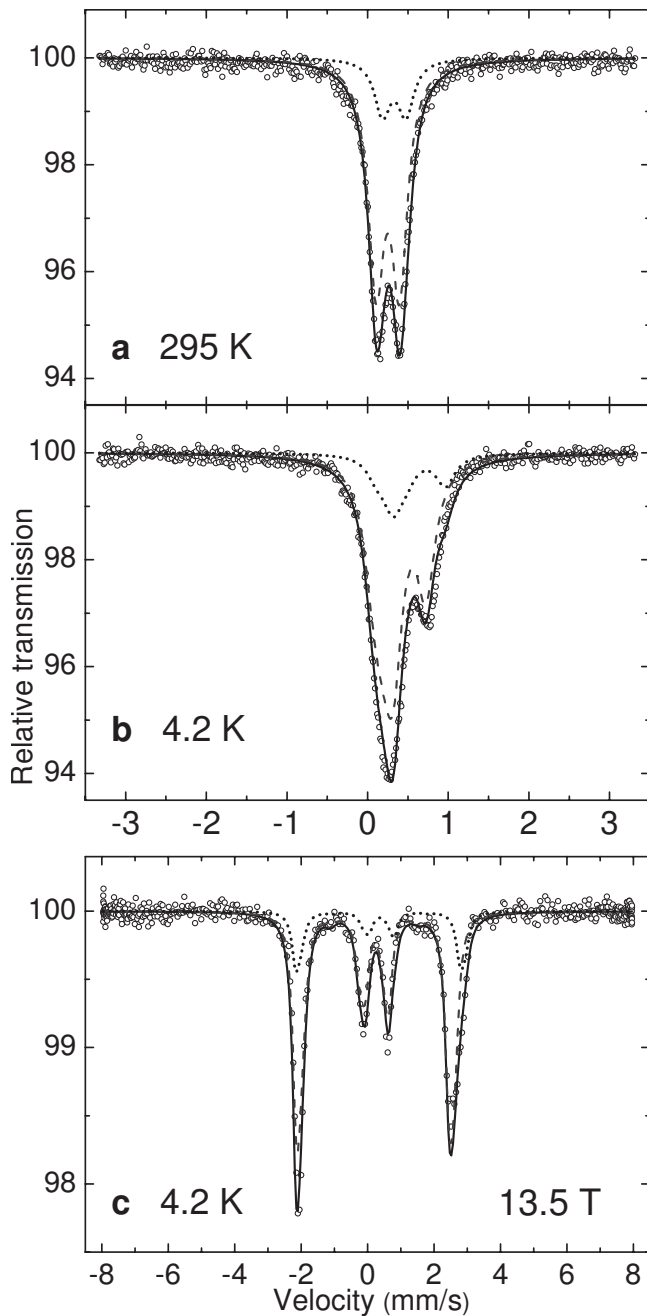


FIG. 8. ⁵⁷Fe Mössbauer spectra recorded in transmission geometry at [(a) and (b)] zero and (c) $\mu_0 H = 13.5$ T external field at various temperatures. The full lines are fits to the data assuming a superposition of two subspectra indicated by dashed (80%) and dotted lines (20% of the total area).

of 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 NaFe₄Sb₁₂ in zero external field, $\mu_0 H_{\text{ind}} = 1.64$ T was found.² Similarly small $\mu_0 H_{\text{ind}}$ values, however, with opposite sign were obtained for Eu_{0.88}Fe₄Sb₁₂.⁴⁰

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

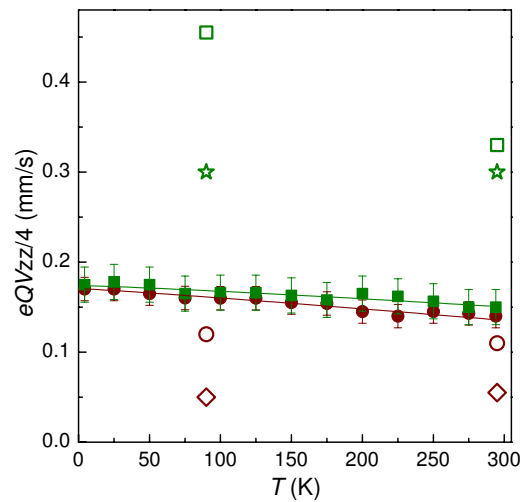


FIG. 9. (Color online) Temperature dependence of the quadrupole splitting $eQV_{zz}/4$ for different Fe atom sites. Full circles (squares), Fe atoms allocated to the spectrum with the large (small) intensity. The lines are guides for the eyes. Values reported by Long *et al.* (Ref. 12) for Tl-deficient Co-containing skutterudites are shown for comparison. Open circles (squares), Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl_{0.8}Co₃FeSb₁₂. Open diamonds (stars), Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl_{0.5}Co_{3.5}Fe_{0.5}Sb₁₂.

shift) by expressing the second order Doppler shift, SOD, via

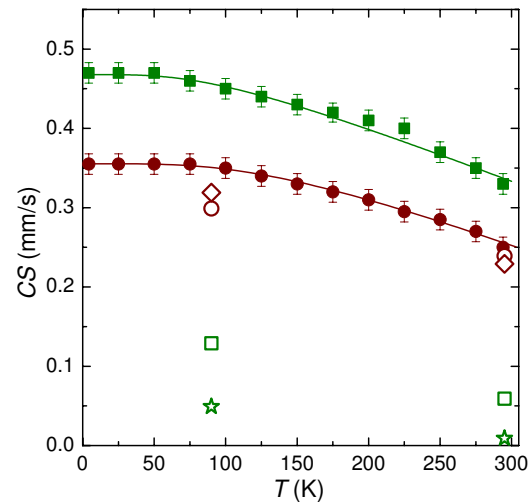


FIG. 10. (Color online) Temperature dependence of the center shift (CS). Full circles (squares), Fe atoms allocated to the spectrum with the large (small) intensity. The lines are fits according to the Debye model. Values reported by Long *et al.* (Ref. 12) for Tl-deficient Co-containing skutterudites are shown for comparison. Open circles (squares), Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl_{0.8}Co₃FeSb₁₂. Open diamonds (stars), Fe atoms allocated to the spectrum with the large (small) intensity recorded for Tl_{0.5}Co_{3.5}Fe_{0.5}Sb₁₂.

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

with $x = \hbar\omega/k_B T$, 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 $\Theta_D = (555 \pm 45)$ K results, $\Theta_D = (350 \pm 40)$ 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 of a specific atom (^{57}Fe) while the latter represents an average for the whole lattice (here, the host structure $[\text{Fe}_4\text{Sb}_{12}]$). Smaller Debye temperatures are also obtained from EXAFS measurements on $\text{CeFe}_4\text{Sb}_{12}$ [$\Theta_D = 390$ K (Ref. 41)], while from Mössbauer investigations a value of 450 K is derived.⁴² 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.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.⁴³ Two subspectra were also obtained for other incompletely filled skutterudites $\text{Pr}_{0.73}\text{Fe}_4\text{Sb}_{12}$ and $\text{Eu}_{0.88}\text{Fe}_4\text{Sb}_{12}$,^{40,44} 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 ^{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 our $\text{TlFe}_4\text{Sb}_{12}$ sample the occupation of the $2a$ site with Tl is high [98(2)%], the probability (in the 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 two, one, and zero Tl atoms, respectively). A similar scenario was suggested for the strongly substoichiometric Co-based Tl skutterudites $\text{Tl}_{0.8}\text{Co}_3\text{FeSb}_{12}$ and $\text{Tl}_{0.5}\text{Co}_{3.5}\text{Fe}_{0.5}\text{Sb}_{12}$ by Long *et al.*,¹² 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 $\text{TlCo}_3\text{FeSb}_{12}$,³² 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. Similarly, the presence of small amounts of Tl^{3+} ions, thus generating a second component in the Fe Mössbauer spectra, is highly unlikely (see discussion in Sec. III A).

IV. CONCLUSIONS

A filled skutterudite with $[\text{Fe}_4\text{Sb}_{12}]$ host and monovalent thallium cation has been synthesized and chemically and structurally characterized. The magnetic, thermal, and ^{57}Fe Mössbauer effect measurements all show that $\text{TlFe}_4\text{Sb}_{12}$ is a weak itinerant electron ferromagnet with $T_C \approx 80$ K, very similar to the isostructural skutterudites with the cations Na^+ and K^+ . 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 $\text{TlFe}_4\text{Sb}_{12}$, 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. ^{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.

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¹A. Leithe-Jasper, W. Schnelle, H. Rosner, N. Senthilkumaran, A. Rabis, M. Baenitz, A. Gippius, E. Morozova, J. A. Mydosh, and Yu. Grin, Phys. Rev. Lett. **91**, 037208 (2003); **93**, 089904(E) (2004).

²A. Leithe-Jasper, W. Schnelle, H. Rosner, M. Baenitz, A. Rabis,

A. A. Gippius, E. N. Morozova, H. Borrmann, U. Burkhardt, R. Ramlau, U. Schwarz, J. A. Mydosh, Yu. Grin, V. Ksenofontov, and S. Reiman, Phys. Rev. B **70**, 214418 (2004).

³G. Sheet, H. Rosner, S. Wirth, A. Leithe-Jasper, W. Schnelle, U. Burkhardt, J. A. Mydosh, P. Raychaudhuri, and Yu. Grin, Phys. Rev. B **72**, 180407(R) (2005).

⁴M. E. Danebrock, C. B. Evers, and W. Jeitschko, J. Phys. Chem. Solids **57**, 381 (1996).

- ⁵W. Schnelle, A. Leithe-Jasper, M. Schmidt, H. Rosner, H. Borrmann, U. Burkhardt, J. A. Mydosh, and Yu. Grin, *Phys. Rev. B* **72**, 020402(R) (2005).
- ⁶J. Sichelschmidt, V. Voevodin, H. J. Im, S. Kimura, H. Rosner, A. Leithe-Jasper, W. Schnelle, U. Burkhardt, J. A. Mydosh, Yu. Grin, and F. Steglich, *Phys. Rev. Lett.* **96**, 037406 (2006).
- ⁷E. Matsuoka, K. Hayashi, A. Ikeda, K. Tanaka, T. Takabatake, and M. Matsumura, *J. Phys. Soc. Jpn.* **74**, 1382 (2005).
- ⁸E. Bauer, S. Berger, A. Galatanu, M. Galli, H. Michor, G. Hilscher, C. Paul, B. Ni, M. M. Abd-Elmeguid, V. H. Tran, A. Grytsiv, and P. Rogl, *Phys. Rev. B* **63**, 224414 (2001).
- ⁹V. V. Krishnamurthy, J. C. Lang, D. Haskel, D. J. Keavney, G. Srajer, J. L. Robertson, B. C. Sales, D. G. Mandrus, D. J. Singh, and D. I. Bilc, *Phys. Rev. Lett.* **98**, 126403 (2007).
- ¹⁰B. C. Sales, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., J.-C. G. Bünzli, and V. K. Pecharsky (Elsevier, Amsterdam, 2003), Vol. 33, Chap. 211, pp. 1–34.
- ¹¹B. C. Sales, B. C. Chakoumakos, and D. Mandrus, *Phys. Rev. B* **61**, 2475 (2000).
- ¹²G. J. Long, B. Mathieu, B. C. Sales, R. P. Hermann, and F. Grandjean, *J. Appl. Phys.* **92**, 7236 (2002).
- ¹³R. P. Hermann, R. Jin, W. Schweika, F. Grandjean, D. Mandrus, B. C. Sales, and G. J. Long, *Phys. Rev. Lett.* **90**, 135505 (2003).
- ¹⁴A. G. Lee, *The Chemistry of Thallium* (Elsevier, New York, 1971).
- ¹⁵J. O. Nriagu, *Thallium in the Environment* (Wiley, New York, 1998).
- ¹⁶C. Recknagel, N. Reinfried, P. Höhn, W. Schnelle, H. Rosner, Yu. Grin, and A. Leithe-Jasper, *Sci. Technol. Adv. Mater.* **8**, 357 (2007).
- ¹⁷STOE WINXPOW, Version 1.2, STOE & Cie GmbH, Darmstadt.
- ¹⁸L. G. Akselrud, P. Y. Zavalii, Yu. Grin, V. K. Pecharsky, B. Baumgartner, and E. Wölfel, *Mater. Sci. Forum* **133-136**, 335 (1993).
- ¹⁹K. Honda, *Ann. Phys.* **32**, 1027 (1910).
- ²⁰S. Mørup and E. Both, *Nucl. Instrum. Methods* **124**, 435 (1975).
- ²¹K. Koepnik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999).
- ²²J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ²³H. Eschrig, *Optimized LCAO Method and the Electronic Structure of Extended Systems* (Springer, Berlin, 1989).
- ²⁴W. Jeitschko and D. Braun, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **B33**, 3401 (1977).
- ²⁵*Chemistry of Aluminium, Gallium, Indium and Thallium*, edited by A. J. Downs (Blackie, London, 1993).
- ²⁶R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **A32**, 751 (1976).
- ²⁷M. D. Hornbostel, E. J. Hyer, J. H. Edvalson, and D. C. Johnson, *Inorg. Chem.* **36**, 4270 (1997).
- ²⁸W. Schnelle, A. Leithe-Jasper, H. Rosner, R. Cardoso-Gil, R. Gumeniuk, J. A. Mydosh, and Y. Grin (unpublished).
- ²⁹T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
- ³⁰The electrical resistivity of polycrystalline samples strongly depends on their porosity, which can be effectively reduced by SPS treatment (see, e.g., Ref. 45).
- ³¹V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Day, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, *Nature (London)* **395**, 876 (1998).
- ³²P. Ghosez and M. Veithen, *J. Phys.: Condens. Matter* **19**, 096002 (2007).
- ³³J. L. Feldman, P. Dai, T. Enck, B. C. Sales, D. Mandrus, and D. J. Singh, *Phys. Rev. B* **73**, 014306 (2006).
- ³⁴C. H. Lee, I. Hase, H. Sugawara, H. Yoshizawa, and H. Sato, *J. Phys. Soc. Jpn.* **75**, 123602 (2006).
- ³⁵M. M. Koza, M. R. Johnson, R. Viennois, H. Mutka, L. Girard, and D. Ravot, *Proceedings of ICT '06, 25th International Conference on Thermoelectrics 2006* (IEEE-CPMT, Piscataway FL, 2007), p. 70.
- ³⁶G. J. Long, R. P. Hermann, F. Grandjean, E. E. Alp, W. Sturhahn, C. E. Johnson, D. E. Brown, O. Leupold, and R. Ruffer, *Phys. Rev. B* **71**, 140302(R) (2005).
- ³⁷J. L. Feldman, D. J. Singh, C. Kendziora, D. Mandrus, and B. C. Sales, *Phys. Rev. B* **68**, 094301 (2003).
- ³⁸H.-C. Wille, R. P. Hermann, I. Sergueev, O. Leupold, P. van der Linden, B. C. Sales, F. Grandjean, G. J. Long, R. Ruffer, and Yu. V. Shvyd'ko, *Phys. Rev. B* **76**, 140301(R) (2007).
- ³⁹M. M. Koza (private communication).
- ⁴⁰M. Reissner, E. Bauer, W. Steiner, G. Hilscher, A. Grytsiv, and P. Rogl, *Physica B* **378-380**, 232 (2006).
- ⁴¹D. Cao, F. Bridges, P. Chesler, S. Bushart, E. D. Bauer, and M. B. Maple, *Phys. Rev. B* **70**, 094109 (2004).
- ⁴²G. J. Long, D. Hautot, F. Grandjean, D. T. Morelli, and G. P. Meisner, *Phys. Rev. B* **60**, 7410 (1999).
- ⁴³J. Steger and E. Kostiner, *J. Solid State Chem.* **5**, 131 (1972).
- ⁴⁴M. Reissner, E. Bauer, W. Steiner, and P. Rogl, *J. Magn. Magn. Mater.* **272-276**, 813 (2004).
- ⁴⁵L. Yang, J. S. Wu, and L. T. Zhang, *J. Alloys Compd.* **364**, 83 (2003).