

## Itinerant iron magnetism in filled skutterudites $\text{CaFe}_4\text{Sb}_{12}$ and $\text{YbFe}_4\text{Sb}_{12}$ : Stable divalent state of ytterbium

W. Schnelle, A. Leithe-Jasper,\* M. Schmidt, H. Rosner, H. Borrmann, U. Burkhardt, J. A. Mydosh,<sup>†</sup> and Y. Grin  
*Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany*

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A comparative study of the filled skutterudite compounds  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CaFe}_4\text{Sb}_{12}$  is presented. Crystal structure investigations and measurements of magnetic susceptibility, specific heat and electrical resistivity in magnetic field, and x-ray absorption spectroscopy have been performed. Almost identical structural, magnetic, and electronic properties of both compounds are observed. Electronic structure calculations support this similarity. It is concluded that ytterbium in  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  is stable divalent and the magnetic moments in both materials are solely due to itinerant-electron paramagnetism of the Fe-Sb polyanion. The calcium and ytterbium iron-antimony skutterudites are nearly ferromagnetic metals and their properties are mainly governed by spin fluctuations.

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Compounds with the filled skutterudite structure are currently under intense investigation due to their wide spectrum of low-temperature ground-state behaviors. While these materials derive from binaries with the general formula  $\text{TX}_3$  ( $T=\text{Co, Rh, Ir}$ ,  $X=\text{P, As, Sb}$ ) the compounds with  $T=\text{Fe, Ru, Os}$  need to be stabilized by a third electropositive element. This leads to filled skutterudites  $\text{R}_y\text{T}_4\text{X}_{12}$ .<sup>1</sup>  $R$  can be chosen among alkaline-earth, rare-earth, actinide metal, or thallium.<sup>2</sup>

For monovalent Na and K in a Fe-Sb host we recently found itinerant ferromagnetism with small ordered magnetic moments ( $\mu_r \approx 0.28\mu_B/\text{Fe atom}$ ) and  $T_C \approx 85$  K. Below  $T_C$   $\text{NaFe}_4\text{Sb}_{12}$  and  $\text{KFe}_4\text{Sb}_{12}$  have a quasi-half-metallic band structure.<sup>3,4</sup> For  $T > T_C$  they display Curie-Weiss-like paramagnetism due to fluctuations of itinerant moments<sup>5</sup> with  $\mu_{\text{eff}}/\text{Fe atom} = 1.6\mu_B$  and  $\Theta \approx T_C$ . The isostructural compounds with divalent cations Ca and Ba show no transitions for  $T > 2$  K.<sup>4</sup> According to fixed spin moment calculations they should also have a ferromagnetic ground state, however, the same strong spin fluctuations as in the Na and K compounds seem to prevent the order.<sup>3,4</sup> This results in nearly ferromagnetic metals with  $\mu_{\text{eff}}/\text{Fe atom} \approx 1.5\mu_B$  and reduced but still positive  $\Theta$  (giving the fluctuation energy<sup>5</sup>):  $\Theta = +50$  K ( $\text{CaFe}_4\text{Sb}_{12}$ ),<sup>4</sup>  $\Theta = +15$  K ( $\text{BaFe}_4\text{Sb}_{12}$ ).<sup>4</sup>

Rare-earth cations ( $R$ ) fitting in the Fe-Sb host's icosahedral void are  $R=\text{La-Eu}$ , and Yb. Some carry a localized magnetic moment rendering the analysis of magnetization intricate, however,  $\text{LaFe}_4\text{Sb}_{12}$  is paramagnetic down to 0.4 K and displays Curie-Weiss behavior with negative  $\Theta \approx -42$  K and reduced  $\mu_{\text{eff}} = 1.13\mu_B$ .<sup>6</sup> Ytterbium is well known for its valence instability, resulting either in the stable valence states  $4f^{13}$  or  $4f^{14}$ , static mixed valency, or intermediate (fluctuating) valency.

$\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  has been characterized as a compound with an intermediate valence of Yb.<sup>7-9</sup> The effective paramagnetic moments  $\mu_{\text{eff}}/\text{f.u.}$  scatter:  $3.09\mu_B$ ,  $\Theta = +40$  K (Ref. 7);  $4.49\mu_B$ ,  $\Theta = +13.8$  K (Ref. 8);  $3.36\mu_B$ ,  $\Theta = +26.5$  K (Ref. 9); and the moment was solely attributed to magnetism of Yb, yet the values are lower than that of the free  $\text{Yb}^{3+}$  ion ( $4.54\mu_B$ ). The temperature dependence of the electrical resistivity and the moderately enhanced linear coefficient  $\gamma$  of the specific heat have been interpreted as due to the Kondo effect and the formation of a heavy fermion state below a coherency temperature  $T^* \approx 50$  K.<sup>7</sup> Additional results,<sup>10,11</sup> including an optical conductivity study, have been interpreted as the appearance of a hybridization gap in a heavy Fermi liquid. However, Bérardan *et al.*<sup>12</sup> recently showed in a study of  $(\text{Ce}_{1-z}\text{Yb}_z)\text{Fe}_4\text{Sb}_{12}$  that Yb contributes only weakly to paramagnetism ( $< 1\mu_B$ ), and that Yb-rich samples show dominantly the  $4f^{14}$  state (i.e.  $\text{Yb}^{2+}$  without a magnetic moment) in x-ray absorption spectra.

In this Rapid communication, we demonstrate that the physical properties of  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  and  $\text{CaFe}_4\text{Sb}_{12}$  filled skutterudites are almost identical. An x-ray absorption spectroscopic (XANES) study of  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  proves unambiguously that Yb is stable divalent. Thus, all magnetic moments in  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  originate solely from the itinerant electron paramagnetism of the Fe-Sb host.

Single crystals of  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  were prepared under argon by recrystallization of a stoichiometric master alloy in a flux of antimony in a glassy carbon crucible. Under argon gas the crucible had been welded in a tantalum container which was then sealed into an evacuated quartz ampoule. The ampoule was heated to 900 °C, slowly cooled to 650 °C within 24 h, and annealed for 7 d. Excess Sb was removed by sublimation in vacuum at 600 °C. Strongly intergrown cubic crystals with edges up to 1.5 mm length could be isolated. The synthesis and characterization of  $\text{CaFe}_4\text{Sb}_{12}$  was already described.<sup>4</sup> The powder was compacted by spark plasma sintering.

All samples were washed in HCl in order to remove secondary phases, especially elemental iron. The residual content of free Fe detected from the field dependence of magnetization at 400 K is  $\approx 10 \mu\text{g/g}$  for both compounds. Magnetization was measured in an MPMS magnetometer in high fields in order to suppress the signal of residual Fe. Magnetization data up to 14 T and heat capacity were obtained in a PPMS. Yb  $L_{\text{III}}$  XANES were taken in transmission geometry at the EXAFS II beamline E4 of HASYLAB at DESY (experimental resolution  $\approx 2$  eV at 8944 eV). The

TABLE I. Crystallographic data of cubic  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  ( $x=0.05(2)$  from crystal structure refinement) at different temperatures. Space group  $Im\bar{3}$ ,  $Z=2$ . Yb is on site  $2a$  (0,0,0), Fe on  $8c$  ( $1/4, 1/4, 1/4$ ), Sb on  $24g$  (0,  $y$ ,  $z$ ). Reliability factors are 2.99%, 4.48%, 4.60%, and 4.45% for 295 K, 200 K, 155 K, and 110 K, respectively.

$T$ (K)	$a$ (Å)	Coordinates		Displacement parameters (Å <sup>2</sup> )		
		$y$	$z$	$B_{\text{Yb}}^{\text{iso}}$	$B_{\text{Fe}}^{\text{iso}}$	$B_{\text{Sb}}^{\text{iso}}$
295	9.1586(8)	0.34031(6)	0.16368(6)	1.70(2)	0.45(2)	0.58(1)
200	9.1431(8)	0.34054(8)	0.16370(9)	1.26(2)	0.41(2)	0.42(2)
155	9.1404(8)	0.34057(8)	0.16364(9)	1.01(2)	0.34(2)	0.34(2)
110	9.1355(8)	0.34055(8)	0.16363(8)	0.75(2)	0.33(2)	0.28(2)

sample was measured simultaneously with  $\text{Yb}_2\text{O}_3$  as an external  $\text{Yb}^{3+}$  reference compound.

To compare the electronic structure of  $\text{CaFe}_4\text{Sb}_{12}$  and  $\text{YbFe}_4\text{Sb}_{12}$ , band-structure calculations using the full-potential nonorthogonal local-orbital (FPLO) calculational scheme<sup>13</sup> within the local density approximation (LDA) have been carried out. As basis set,  $\text{Ca}(3s, 3p, 4s, 4p, 3d)$ ,  $\text{Yb}(4f, 5s, 5p, 6s, 6p, 5d)$ ,  $\text{Fe}(3s, 3p, 4s, 4p, 4d)$ , and  $\text{Sb}(4s, 4p, 4d, 5s, 5p, 5d)$  states were employed. The strongly correlated Yb  $4f$  states were treated using an additional Coulomb repulsion  $U$  within the LDA+ $U$  scheme. Further details are given in Ref. 4.

For  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$ , wavelength dispersive electron microprobe analysis of selected crystals resulted in a composition  $\text{Yb}_{0.97(1)}\text{Fe}_{3.98(2)}\text{Sb}_{12.04(4)}$  while ICP-OS chemical analysis gave  $\text{Yb}_{0.95(2)}\text{Fe}_{3.99(6)}\text{Sb}_{12.1(2)}$ . Both results indicate a small deficit ( $x$ ) of Yb, in good agreement with the crystal structure refinement. For  $\text{CaFe}_4\text{Sb}_{12}$  the analyses consistently yielded full occupancy for Ca.

Both compounds crystallize with the  $\text{LaFe}_4\text{P}_{12}$  type of structure<sup>1</sup> with cubic lattice parameters (at 300 K)  $a=9.1586(8)$  Å for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  [cf. 9.158(1) Å, Ref. 7; 9.1571(5) Å, Ref. 8] and 9.1634(4) Å for  $\text{CaFe}_4\text{Sb}_{12}$ , respectively. There is no change of the structure down to 110 K, however, the large displacement parameter of Yb  $B_{\text{Yb}}^{\text{iso}}$  decreases strongly (see Table I).

The magnetic susceptibilities of a  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  single crystal and of  $\text{CaFe}_4\text{Sb}_{12}$  powder are displayed in Fig. 1. The susceptibilities for  $T > 100$  K are almost identical: fits with a Curie-Weiss law (range  $150 \text{ K} < T < 400 \text{ K}$ ) yield effective moments  $\mu_{\text{eff}}/\text{Fe atom}$  of  $1.50\mu_B$  and  $\Theta = +49 \text{ K}$  for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  (in reasonable agreement with Ref. 7) and  $1.51\mu_B$ ,  $+49 \text{ K}$  for  $\text{CaFe}_4\text{Sb}_{12}$ . Higher values of  $\mu_{\text{eff}}/\text{Fe atom}$  previously reported<sup>8</sup> for the Yb compound are probably due to undetected phases containing  $\text{Yb}^{3+}$ , e.g.,  $\text{Yb}_2\text{O}_3$ .<sup>12</sup> Only below 100 K has the Yb compound a slightly larger paramagnetism than the Ca compound. The shoulder in  $M/H$  around  $50 \text{ K} \approx \Theta$  is present in both compounds and for both fields (Fig. 1). With decreasing temperature  $M/H$  again increases and then saturates for  $T < 5 \text{ K}$  and  $H = 7 \text{ T}$ . This characteristic behavior persists in fields up to 14 T. For fields  $H \leq 0.1 \text{ T}$  strong upturns of  $M/H$  are observed for  $T \leq 20 \text{ K}$ .<sup>4</sup> A similar temperature and field dependence of  $M/H$  was observed for  $\text{BaFe}_4\text{Sb}_{12}$  [ $\mu_{\text{eff}}/\text{Fe atom} = 1.57\mu_B$ ,  $\Theta = +15.0(9) \text{ K}$ ] where only  $\Theta$  is significantly

smaller.<sup>4</sup> These features are due to incipient ferromagnetism and the concomitant strong spin fluctuations in these  $[\text{Fe}_4\text{Sb}_{12}]$  skutterudites with divalent cations.<sup>3,4</sup>

The specific heat of  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  is plotted along with that of  $\text{CaFe}_4\text{Sb}_{12}$  in Fig. 2 for  $T < 14 \text{ K}$ .  $c_p(T)$  of both compounds is well described by the sum of a large electronic term  $\gamma T$  and phonon terms.<sup>14</sup> In order to account for the thermal excitations of the loosely bonded cation an Einstein term (characteristic temperature  $\Theta_E$ ) for the  $1-x$  atoms on this site needs to be combined with a Debye model (Debye temperature  $\Theta_D$ ) for the 16 atoms of the polyanion. Clearly, there are contributions to  $c_p(T)$  of higher power than  $\beta T^3$ , however, the  $\delta T^5$  term of the Debye model is of equal importance for temperatures where the Einstein term becomes significant. Due to the strong numerical interdependence with  $\delta$ , the filling factor was set as determined by chemical analysis. For  $H=0$  a fit (range 5 K–14 K; cf. Ref. 14) yields for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  [ $\text{CaFe}_4\text{Sb}_{12}$ ; range of fit 1.8 K–14 K]:  $\gamma = 138.1(1.1)$  [ $109.1(0.4)$ ]  $\text{mJ mol}^{-1} \text{K}^{-2}$ ,  $\beta$  corresponding to  $\Theta_D = 258$  [268] K for 16 atoms,  $\delta = 0$  [0.53(5)]  $\mu\text{J mol}^{-1} \text{K}^{-6}$ , and  $\Theta_E = 63.0(3)$  [87.8(4)] K. For both compounds enhanced  $\gamma$  values are observed, the value for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  being in accordance with Ref. 7.

Interestingly, for  $\text{LaFe}_4\text{Sb}_{12}$  an even larger  $\gamma$  is reported<sup>6,15</sup> ( $195 \text{ mJ mol}^{-1} \text{K}^{-2}$ , Ref. 16). The isostructural

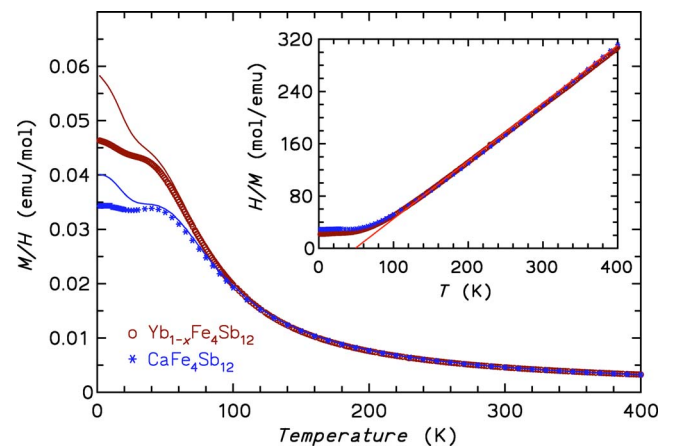


FIG. 1. (Color online) Magnetic susceptibility  $M/H$  for  $H=7 \text{ T}$  (symbols) and  $3.5 \text{ T}$  (lines). The inset displays inverse susceptibility  $H/M$  for  $H=7 \text{ T}$  and a Curie-Weiss fit for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  (straight line, see text).

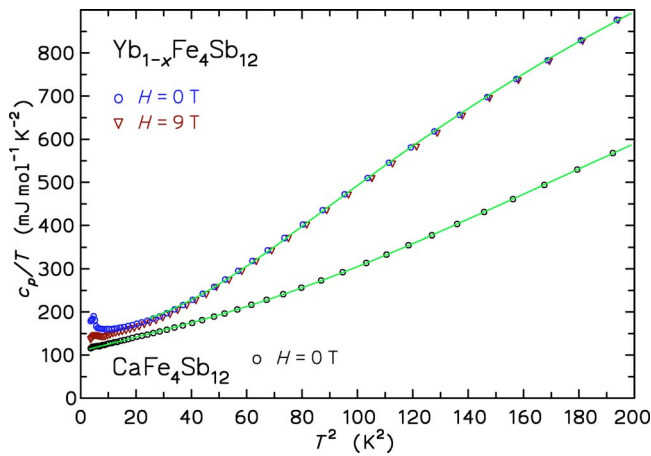


FIG. 2. (Color online) Specific heat at low  $T$  plotted  $c_p/T$  vs  $T^2$ . For  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  data for  $H=9$  T are also shown. The lines display the fits (see text).

compounds with Na, K (ferromagnets), and Ba (nearly ferromagnetic) have  $\gamma$  of 100–120  $\text{mJ mol}^{-1}\text{K}^{-2}$  (Refs. 3 and 16). It has to be concluded that the large  $\gamma$  is a general electronic property of the  $[\text{Fe}_4\text{Sb}_{12}]$  polyanion and not at all unique to rare-earth filled compounds. The Wilson ratio  $R_W = \pi^2 k_B^2 \chi / 3 \mu_B^2 \gamma$  at low  $T$  is  $\approx 24$  for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  and  $\text{CaFe}_4\text{Sb}_{12}$ , indicating that they are close to a quantum critical point (QCP).<sup>17</sup>

Our fitted  $\Theta_E$  for the Yb atom is somewhat lower than that from a recent EXAFS study (72 K, Ref. 18), but slightly larger than the value for thallium in  $\text{Tl}_{0.8}\text{Co}_4\text{Sb}_{11}\text{Sn}$  (53 K, Ref. 19) scaled by the square root of the atomic masses (giving 58 K). Using  $\Theta_E$  and  $m = M_{\text{Yb}}$  in an Einstein oscillator [cf. Ref. 20, Eq. (2)] we obtain values of  $B_{\text{Yb}}^{\text{iso}}$  close to those from our diffraction data (e.g. at 300 K  $1.72\text{\AA}^2$ , cf. Table I). The  $\Theta_D$  (characterizing the elastic properties of the host structure) for  $\text{CaFe}_4\text{Sb}_{12}$  and  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  are also similar.

The electronic state (valence) of ytterbium in  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  was investigated by XANES. The spectrum (Fig. 3) is dominated by a maximum shifted 8 eV lower than the maximum of  $\text{Yb}^{3+}$  ( $4f^{13}$ ). This line for  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  is attributed to the  $4f^{14}$  configuration of  $\text{Yb}^{2+}$ . A shoulder in the spectrum indicates that the sample contains a small amount of  $4f^{13}$  configuration ( $\text{Yb}^{3+}$ ). Evaluation by fitting two main Lorenz-like peaks plus two threshold functions results in an effective Yb valence  $\nu = 2.10 \pm 0.05$ . A similar value  $\nu = 2.16$  was recently obtained by Bérardan *et al.*<sup>12</sup> on a sample of composition  $\text{Yb}_{0.93}\text{Fe}_4\text{Sb}_{12.08}$ . Our preliminary data at pressures up to 7 GPa did not reveal a significant change of the XANES, thus the Yb valence is quite stable in  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$ . The residual difference of  $\nu$  to the integral value two as well as the observation of mixed valence ( $\nu = 2.68$ ) by XANES in Ref. 8 is probably due to  $\text{Yb}_2\text{O}_3$  contamination.<sup>12</sup> In this context the question arises whether the valence of Yb is still stable with significantly larger  $x$  (cf. Ref. 21).

Electrical resistivity  $[\rho(T)]$  and magnetoresistivity ratio (MR) data are given in Fig. 4. A large positive MR of 30% and 20%, respectively, in  $H=9$  T is observed for  $T < 40$  K, as in Refs. 9 and 10. Its origin is probably classical with the large magnitude due to the low carrier concentrations, espe-

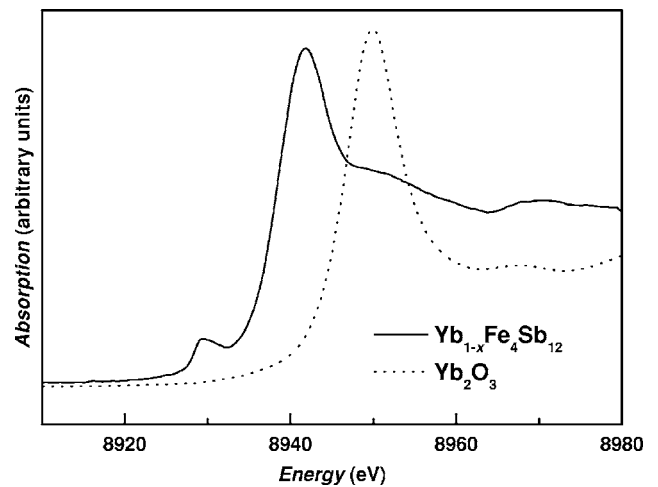


FIG. 3. X-ray absorption spectra of  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  and of  $\text{Yb}_2\text{O}_3$  at the ytterbium  $L_{\text{III}}$  edge at room temperature.

cially at low  $T$ .<sup>16</sup> Between 35 K and 125 K the MR is negative for the  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  crystal. The MR of  $\text{CaFe}_4\text{Sb}_{12}$  shows only a minimum at these temperatures but remains positive up to 320 K, similar to Na and K filled skutterudites.<sup>16</sup> The negative MR contribution at  $T \approx \Theta$  correlates with the local maximum in  $\chi(T)$  and is probably a signature of spin fluctuations.<sup>5</sup> An analysis of transport data is hampered by sample dependence: While our  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  crystal has  $\rho(300\text{ K}) \approx 315 \mu\Omega\text{ cm}$ , in Ref. 10 for  $\text{YbFe}_4\text{Sb}_{12}$  a value  $> 3\text{ m}\Omega\text{ cm}$  is found. The common feature, however, is the broad shoulder in  $\rho(T)$  at 60–80 K which is an indication for narrow-band scattering near the Fermi level. The overall resistivity and MR features of both compounds are similar, indicating similarly structured Fermi surfaces.

The electronic structure for  $\text{YbFe}_4\text{Sb}_{12}$  was calculated for different representative values of  $U$ . First, the value 8 eV was adopted from the energy shift of the XANES peak of the skutterudite with respect to  $\text{Yb}_2\text{O}_3$ , and then alternatively,  $U=4, 6$ , and 10 eV. Except for the  $4f$  electrons, the resulting

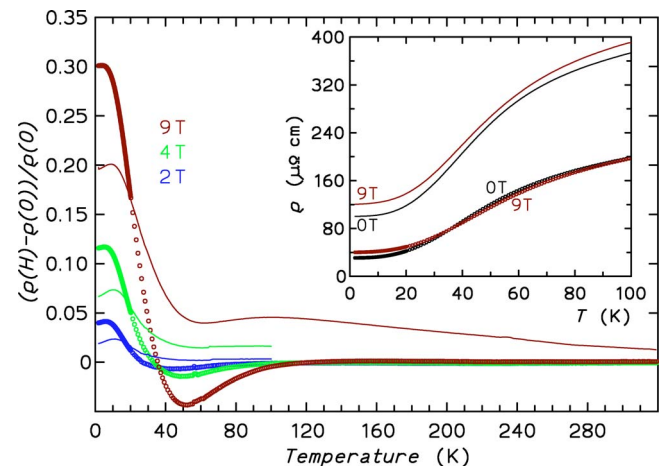


FIG. 4. (Color online) Transverse magnetoresistivity ratio for single crystalline  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  (symbols) and polycrystalline  $\text{CaFe}_4\text{Sb}_{12}$  (lines) for  $H=9$  T (topmost curves), 4 T, and 2 T. The inset shows electrical resistivity in zero and 9 T field.

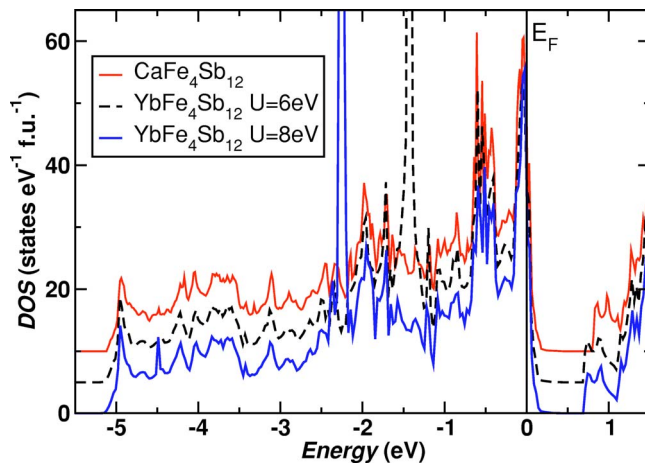


FIG. 5. (Color online) Total electronic density of states for  $\text{YbFe}_4\text{Sb}_{12}$  calculated for two different values of  $U$  and for  $\text{CaFe}_4\text{Sb}_{12}$ . Curves have been shifted for clarity by five units.

band structures differ only in small details from that of  $\text{CaFe}_4\text{Sb}_{12}$ . The influence of different  $U$  on the total density of states (DOS; see Fig. 5) is only a shift in the energy of the  $4f$  peak in  $\text{YbFe}_4\text{Sb}_{12}$ , which for all  $U$  negligibly contributes to the DOS at  $E_F$ . Otherwise, there are simply minor differences between the DOS curves. The DOS at  $E_F$  are 32 and 31 states  $\text{eV}^{-1}\text{f.u.}^{-1}$  for  $\text{CaFe}_4\text{Sb}_{12}$  and  $\text{YbFe}_4\text{Sb}_{12}$ , respectively, independent of  $U$ . This yields a “bare”  $\gamma \approx 75 \text{ mJ mol}^{-1} \text{K}^{-2}$ , when compared to the measured  $\gamma$  a not

unusually large renormalization results. Fixed spin moment calculations,<sup>3</sup> which neglect quantum spin fluctuations, predict for both compounds a magnetization of  $0.5 \mu_B/\text{Fe}$  atom.

In conclusion, the electronic state of ytterbium in  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  filled skutterudite was shown to be  $4f^{14}$ . The origin of the enhanced paramagnetism and electronic specific heat at low temperatures is the magnetism of the host anion  $[\text{Fe}_4\text{Sb}_{12}]$  to which a charge  $-(2-2x)$  is transferred from the cation. This itinerant electron paramagnetism<sup>5</sup> of  $\text{CaFe}_4\text{Sb}_{12}$  and  $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$  is characterized by a positive Weiss temperature  $\Theta \approx 50 \text{ K}$  without long-range ferromagnetic order. As concluded from electronic structure calculations, these skutterudites with divalent fillers are nearly ferromagnetic. Characteristic anomalies in the magnetization at  $T \approx \Theta$  and a negative magnetoresistance contribution are signatures of strong spin fluctuations. The large Wilson ratio ( $\approx 24$ ) demonstrates that they are close to the ferromagnetic instability (QCP). Thus, the scenario of the hybridization gap model appropriate for localized  $4f$  Yb moments<sup>11</sup> is unlikely, especially in view of the nearly identical behavior of  $\text{CaFe}_4\text{Sb}_{12}$ . However, the presence of a narrow feature near  $E_F$  is indicated by the shoulder in  $\rho(T)$  of both compounds, consequently, narrow or renormalized  $d$  bands may be the cause for this behavior.

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\*Electronic address: jasper@cpfs.mpg.de

†Permanent address: Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands.

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