



MAGNETIC PROPERTIES OF ALKALINE EARTH AND LANTHANOID IRON ANTIMONIDES $\text{AFe}_4\text{Sb}_{12}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{La-Nd}, \text{Sm}, \text{Eu}$) WITH THE $\text{LaFe}_4\text{P}_{12}$ STRUCTURE

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Abstract—The magnetic properties of the nine title compounds were studied by magnetic susceptibility measurements with a SQUID magnetometer between 2 and 300 K. At temperatures above 100 K, all compounds with the exception of the cerium and samarium compounds show Curie–Weiss behaviour. The effective magnetic moments of the alkaline earth compounds vary between $3.7 \pm 0.2 \mu_B$ and $4.0 \pm 0.2 \mu_B$ per formula unit. For $\text{LaFe}_4\text{Sb}_{12}$ the moment is smaller ($3.0 \pm 0.2 \mu_B$) indicating a higher degree of electronic saturation within the $\text{Fe}_4\text{Sb}_{12}$ polyanion. At lower temperatures, the magnetic susceptibilities of these compounds deviate from the Curie–Weiss law, however, they remain field independent. A mixed valent behaviour is observed for the cerium compound and the samarium compound reflects the Van Vleck paramagnetism of the Sm^{3+} ions. The magnetic susceptibilities of the other lanthanoid compounds correspond to the sums of the susceptibilities of the $\text{Fe}_4\text{Sb}_{12}$ polyanion and the Ln^{3+} and Eu^{2+} ions, respectively. These antimonides order ferromagnetically with Curie temperatures varying between 5(1) K for $\text{PrFe}_4\text{Sb}_{12}$ and 82(2) K for $\text{EuFe}_4\text{Sb}_{12}$. The magnetic properties of these compounds are discussed within the framework of a rigid band structure.

Keywords: A. magnetic materials, D. electronic structure, D. magnetic properties.

1. INTRODUCTION

The ternary lanthanoid transition metal pnictides $\text{LnT}_4\text{Pn}_{12}$ (Ln = early lanthanoids including La, T = Fe, Ru, Os; Pn = P, As, Sb) with the cubic $\text{LaFe}_4\text{P}_{12}$ type structure (Fig. 1) have been known for some time [1–3]. It has also been shown, that the lanthanoid components can be substituted by the actinoids thorium and uranium [4, 5] or by alkaline earth elements [6, 7]. Some additional rare earth transition metal antimonides were reported recently [8].

The crystal structure of these compounds can be derived from the binary mineral skutterudite (CoAs_3), which occurs for all nine combinations of the transition metals T = Co, Rh, and Ir with the pnictogens Pn = P, As and Sb [9–11]. These compounds are diamagnetic semiconductors or semimetals [12–14], while the isotypic phosphide NiP_3 —with one additional electron per formula unit—is a good metallic conductor [15–17]. The formula of these binary pnictides may be written as $\square\text{T}_4\text{Pn}_{12}$, where the symbol \square indicates a relatively large void, which is filled by electropositive elements in the ternary compounds. A binary compound FeP_3 ($\square\text{Fe}_4\text{P}_{12}$) does not exist, however the polyanion $[\text{Fe}_4\text{P}_{12}]^{4-}$ occurs in the ternary compound $\text{ThFe}_4\text{P}_{12}$ [4]. It can be expected that this compound—where thorium is undoubtedly

tetravalent—is semiconducting. Semiconducting behaviour was observed for $\text{CeFe}_4\text{P}_{12}$ [5, 18, 19], $\text{CeFe}_4\text{As}_{12}$ [18] and $\text{UFe}_4\text{P}_{12}$ [5], while the electron deficient compounds $\text{LaFe}_4\text{Pn}_{12}$ (Pn = P, As, Sb) [18], $\text{PrFe}_4\text{P}_{12}$ [19] and $\text{EuFe}_4\text{P}_{12}$ [18] are metallic conductors. $\text{LaFe}_4\text{P}_{12}$, $\text{LaRu}_4\text{P}_{12}$ and $\text{LaOs}_4\text{P}_{12}$ are even superconductors with transition temperatures of $T_c = 4.1$ K [20, 21], $T_c = 7.2$ K [20] and $T_c = 1.8$ K [22], respectively. The ^{57}Fe Mössbauer spectra of several rare earth iron pnictides $\text{LnFe}_4\text{Pn}_{12}$ were studied [18, 23] and the ^{151}Eu spectra of $\text{EuFe}_4\text{P}_{12}$ reveal a giant hyperfine field on the europium atoms [24]. X-Ray absorption near-edge spectroscopy (XANES) studies revealed a complex behaviour of the cerium atoms in $\text{CeFe}_4\text{P}_{12}$ [25]. Chemical bonding in the binary pnictides TPn_3 and the filled ternary ones $\text{LnT}_4\text{Pn}_{12}$ was rationalized on the basis of simple models [1, 14, 18, 26] and by extended Hückel calculations [27].

The magnetic susceptibility of $\text{CeFe}_4\text{P}_{12}$ was found to be small [5, 18], indicating a high degree of electronic saturation of the $[\text{Fe}_4\text{P}_{12}]^{4-}$ polyanion. Nevertheless, the cerium atoms in this compound seem to have some intermediate valence character [5, 18, 25] and for the interpretation of its semiconductivity the interactions of the cerium atoms with the three-dimensionally infinite iron–phosphorus polyanion seem to be important [18, 25]. In the corresponding phosphide $\text{LaFe}_4\text{P}_{12}$,

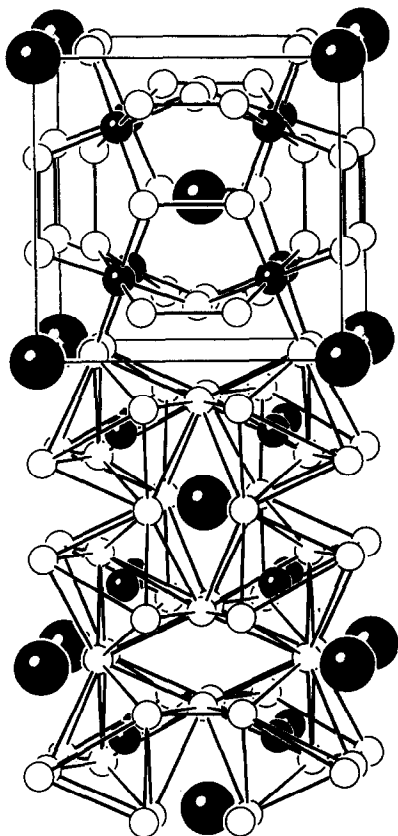


Fig. 1. Crystal structure of the $\text{LaFe}_4\text{P}_{12}$ type antimonides $\text{AFe}_4\text{Sb}_{12}$ ($A = \text{Ca, Sr, Ba, La-Nd, Sm, Eu}$). Large and small black spheres represent the A and Fe atoms, respectively. The cubic cell is outlined in the upper part of the figure, below which the octahedral antimony coordination of the iron atoms is emphasized.

however, the polyanion $[\text{Fe}_4\text{P}_{12}]^{3-}$ is undoubtedly electronically unsaturated; this compound has metallic conductivity and a higher susceptibility [18, 21], which is nearly temperature independent, and this behaviour can be interpreted as being Pauli paramagnetic. In any case, the magnetic susceptibilities of $\text{LaFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ are small and the iron sublattices of these phosphides do not seem to carry localized magnetic moments. In contrast, relatively large magnetic moments are found for the polyanions of all the corresponding iron antimonides reported here.

2. SAMPLE PREPARATION

The ternary antimonides were prepared by reaction of the binary alkaline earth and rare earth antimonides with iron and antimony. Starting materials were granules of calcium (Ventron, > 99.5%), ingots of strontium (Ventron, m2n), barium (Ventron, > 99.5%) and the rare earth metals (purity > 99.9%), powders of iron (Merck, reinst) and antimony (Ventron, N2m5). Filings of the alkaline earth and the rare earth metals were prepared under argon. They were annealed with

the appropriate amounts of antimony in evacuated, sealed silica tubes for two days at 450°C followed by five days at 750°C . The resulting antimonides CaSb_2 , SrSb_2 , BaSb_3 , LnSb ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm}$) and EuSb_2 , were essentially single-phase. They were ground together with the transition metals and antimony, pressed to pellets and sealed in evacuated silica tubes, which had been annealed before under vacuum to eliminate traces of water. The best results were obtained with starting compositions corresponding to $\text{Ln}:\text{Fe}:\text{Sb} = 2:4:13$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm}$), $\text{A}:\text{Fe}:\text{Sb} = 2:4:14$ ($A = \text{Ca, Sr, Eu}$) and $\text{Ba}:\text{Fe}:\text{Sb} = 2:4:15$. The samarium compound $\text{SmFe}_4\text{Sb}_{12}$ is thermodynamically stable only in a rather limited temperature range. It was prepared by heating the components quickly to 640°C and holding them at this temperature for 24 h, followed by quenching in water. The other samples were quickly heated to 660°C , kept at this temperature for 3 h, cooled by 1°C/h to 600°C and quenched in water. The excess antimony as well as the binary alkaline earth and rare earth antimonides were removed by treating the products with concentrated hydrochloric acid for several minutes (the alkaline earth compounds), or for one day (those with the rare earth elements). After these procedures the ternary antimonides were about 90% single-phase with the Pauli paramagnetic antimonide FeSb_2 [28] as the only impurity detected from the Guinier powder diagrams, and this was accounted for during the evaluation of the magnetic data.

3. MAGNETIC INVESTIGATIONS

The magnetic measurements were carried out with a SQUID magnetometer (Quantum Design Inc.) in the temperature range between 2 and 300 K and with flux densities in the range of $\pm 5.5\text{ T}$. The samples had weights between 4 and 20 mg. They were enclosed in thin-walled silica tubes of about 1 mm diameter. Usually the samples were cooled in zero field to about 20 K and slowly heated to room temperature in magnetic fields of 1, 3, 4 and 5 T to check for ferromagnetic impurities. Very small amounts of such impurities were frequently observed, however these amounts were in all cases so small that the susceptibilities obtained at 3, 4 and 5 T were the same and for that reason only those obtained at 3 T are reported. To investigate the ordering phenomena of the magnetic rare earth iron antimonides, the samples were slowly cooled from temperatures somewhat above the expected Curie temperatures in a magnetic field of 0.1 T.

4. RESULTS AND DISCUSSION

As mentioned above, the structure of the ternary $\text{LaFe}_4\text{P}_{12}$ type compounds may be regarded as a

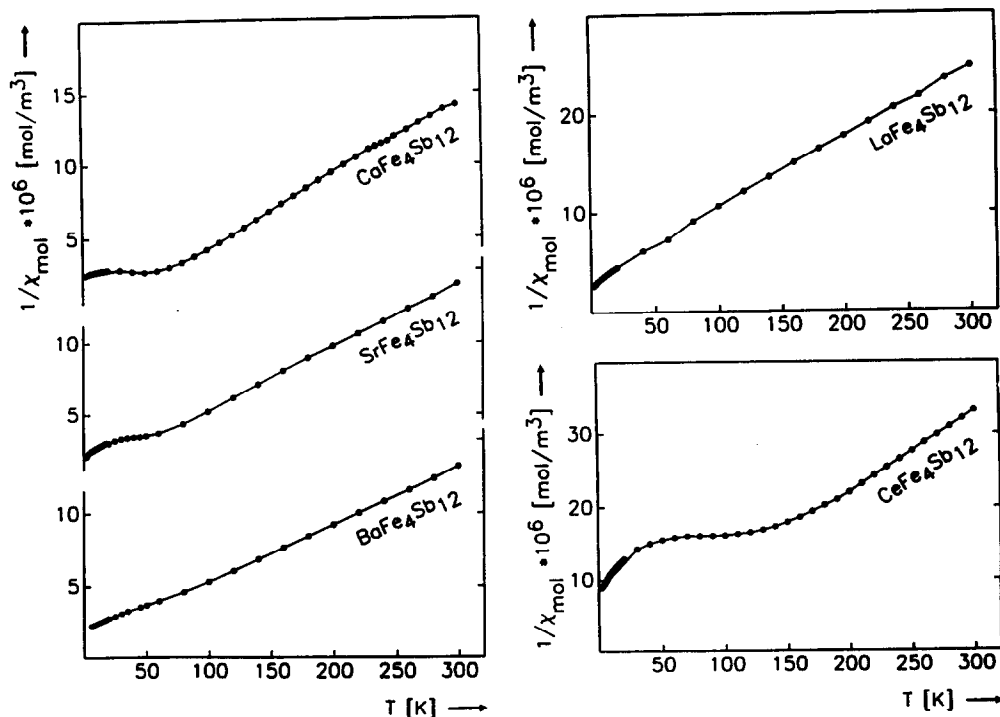


Fig. 2. Temperature dependence of the reciprocal magnetic susceptibilities χ^{-1} of the ternary antimonides $A\text{Fe}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}, \text{La}$ and Ce) measured in a magnetic field of 3 T.

filled-up version of the binary skutterudite CoAs_3 ($\text{Co}_4\text{As}_{12}$) type structure. The isotypic binary cobalt antimonide CoSb_3 is also known. This compound is electronically saturated as is indicated by its diamagnetism and its semimetallic behaviour [14]. Chemical bonding may be rationalized by a simple bonding model, where two electrons are counted for each near-neighbour interaction [1, 14, 18]. The antimony atoms form four-membered rings. Thus, each antimony has two antimony neighbours, and assuming that the antimony atoms obey the octet rule, they obtain the oxidation number -1 , in agreement with the Zintl-Klemm concept [29–32]. Accordingly, the formula of CoSb_3 may be expressed by $\text{Co}^{3+}(\text{Sb}^{1-})_3$ or—in emphasizing the Sb_4 -rings— $(\text{Co}^{3+})_4[(\text{Sb}^{1-})_4]_3$. The cobalt atoms obtain the oxidation number $+3$, i.e. a d^6 system.* They have six antimony neighbours in octahedral coordination (“ d^2sp^3 hybrid”). In counting two electrons for each of these interactions, we realize that they obey the 18-electron rule. The six nonbonding electrons of the d^6 system may be accommodated in the d_{xy} , d_{xz} and d_{yz} orbitals, and this is generally called a low spin d^6 system, which is in

agreement with the diamagnetism of CoSb_3 . In a hypothetical compound FeSb_3 ($\text{Fe}_4\text{Sb}_{12}$), each iron atom could be expected to have a d^5 system with one unpaired electron per iron atom and this is to some extent reflected by the magnetic behaviour of the ternary compounds.

We will first discuss the magnetic susceptibility behaviour of the $A\text{Fe}_4\text{Sb}_{12}$ compounds with non-magnetic A components ($A = \text{Ca}, \text{Sr}, \text{Ba}$ and La). At temperatures above 200 K these antimonides show Curie–Weiss behaviour (Fig. 2). The effective magnetic moments μ_{exp} , calculated from the slope of the $1/\chi$ vs T plots are listed in Table 1. For the alkaline earth compounds these moments vary between 3.7 and $4.0 \mu_B$ /formula unit with estimated error limits of $0.2 \mu_B$. For $\text{LaFe}_4\text{Sb}_{12}$ the magnetic moment is lower with $\mu_{\text{exp}} = 3.0 \pm 0.2 \mu_B/\text{f.u.}$ This is in qualitative agreement with the simple band structure discussed above, since the alkaline earth atoms (e.g. Ca) are expected to transfer two electrons per formula unit to the iron–antimony polyanion, while the lanthanum atoms are expected to transfer three electrons according to the formulas $\text{Ca}^{2+}(\text{Fe}_4\text{Sb}_{12})^{2-}$ and $\text{La}^{3+}(\text{Fe}_4\text{Sb}_{12})^{3-}$. Thus, in the calcium compound two out of four iron atoms could be expected to carry uncompensated spins, while in the lanthanum compound only one iron atom per f.u. should have a magnetic d^5 system. Therefore the expected moments calculated from the Curie–Weiss law $\mu_{\text{exp}} = 2.83 [(\chi/n)(T - \Theta)]^{1/2}$ should be in the ratio of $\sqrt{2}:1$, since $n = 2$ for the alkaline

*In calculating oxidation numbers (formal charges) shared electrons are always counted at the more electronegative partner, i.e. oxidation numbers are usually integers, regardless of the partial covalent character of the bonding electrons. Sometimes oxidation numbers and ionic charges are noted differently, e.g. Co^{3+} and Co^{+3} . For simplicity we make no distinction between oxidation numbers and ionic charges.

Table 1. Magnetic properties of the antimonides $\text{AFe}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}, \text{La-Nd}, \text{Sm}, \text{Eu}$)^a

Compound	m	μ_{exp} (μ_B)/f.u.	$\mu_{\text{exp(Fe)}}$ (μ_B)/"Fe ³⁺ "	$\mu_{\text{exp(A)}}$ (μ_B)/A	μ_{eff} (μ_B)	Θ (K)	T_c (K)	Magnetic behaviour of the A component
$\text{CaFe}_4\text{Sb}_{12}$	2	3.7(2)	2.6(1)	—	—	3(1)	—	nonmagnetic
$\text{SrFe}_4\text{Sb}_{12}$	2	3.8(2)	2.7(1)	—	—	-17(1)	—	nonmagnetic
$\text{BaFe}_4\text{Sb}_{12}$	2	4.0(2)	2.8(1)	—	—	-36(1)	—	nonmagnetic
$\text{LaFe}_4\text{Sb}_{12}$	1	3.0(2)	3.0(1)	—	—	-51(1)	—	nonmagnetic
$\text{CeFe}_4\text{Sb}_{12}$	0.4	2.4(2)	—	—	2.54 (Ce ³⁺)	1(1)	—	0.4 Ce ³⁺ /0.6 Ce ⁴⁺
$\text{PrFe}_4\text{Sb}_{12}$	1	4.6(2)	(3.0)	3.5(2) ^b	3.58 (Pr ³⁺)	-22(1)	5(2)	ferromagnetic
$\text{NdFe}_4\text{Sb}_{12}$	1	4.5(2)	(3.0)	3.4(2) ^b	3.62 (Nd ³⁺)	-15(1)	13(1)	ferromagnetic
$\text{SmFe}_4\text{Sb}_{12}$	1	—	(3.0)	1.6(2) ^b	1.66 (Sm ³⁺)	—	45(2)	ferromagnetic
$\text{EuFe}_4\text{Sb}_{12}$	2	8.4(2)	(2.6)	6.8(2) ^b	7.94 (Eu ²⁺)	-13(1)	82(2)	ferromagnetic

^aIn the second column the number m of formally unpaired electrons in the $[\text{Fe}_4\text{Sb}_{12}]^{(4-m)-}$ polyanion is listed. The total magnetic moments μ_{exp} as obtained from the Curie-Weiss law are split into a part $\mu_{\text{exp(Fe)}}$, accounting for the moments of the polyanion, and a part $\mu_{\text{exp(A)}}$, accounting for the moments of the A components. The theoretical effective moments μ_{eff} for the rare earth ions are listed for comparison. For the samarium compound the values of $\mu_{\text{exp(A)}}$ and μ_{eff} correspond to the Van Vleck paramagnetism at room temperature. The Weiss constants Θ and the Curie temperatures T_c are also given.

^bAfter subtraction of the susceptibility of the $[\text{Fe}_4\text{Sb}_{12}]$ sublattice (the susceptibility values corresponding to the magnetic moments $\mu_{\text{exp(Fe)}}$ listed in the fourth column).

earth compounds and $n = 1$ for the lanthanum compound. This is approximately observed with the experimental moments of 3.7–4.0 μ_B /f.u. for the alkaline earth compounds and 3.0 μ_B /f.u. for the lanthanum compound. Alternatively, calculated per Fe³⁺ of the f.u., we obtain the values (dividing by $\sqrt{2}$) of 2.6–2.8 μ_B for the alkaline earth compounds. The value of 3.0 μ_B for the lanthanum compound agrees rather well with these values, if we consider that the magnetic moment for the lanthanum compound was calculated for the ideal formula. In reality, the structure refinements for $\text{LaFe}_4\text{Sb}_{12}$ [3] and $\text{NdFe}_4\text{Sb}_{12}$ [8] resulted in occupancy parameters of $93.9 \pm 1.3\%$ and $83.2 \pm 0.7\%$ for the rare earth positions. If such defects are taken into account, a larger percentage of the iron atoms in $\text{LaFe}_4\text{Sb}_{12}$ will remain with uncompensated spins, which allows to rationalize the higher magnetic moment of 3.0 μ_B .

According to the formula $\mu_{\text{eff}} = 2[s(s+1)]^{1/2} \mu_B$, a magnetic moment of 1.73 μ_B should be expected for the spin-only value of a Fe³⁺ ion with a low spin d^5 system containing one unpaired electron. The values of about 2.7 μ_B observed by us for the ternary antimonides are considerably higher. This, however, is also the case for many other low spin Fe³⁺ compounds, e.g. for alkaline earth hexacyanoferrates(III) $\text{A}_3[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) and $\text{A}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ ($A = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) magnetic moments between 2.19 and 2.39 μ_B were observed [33]. For the corresponding rare earth compounds $\text{A}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($A = \text{Sc}, \text{Y}, \text{La}$) the moments are generally higher and vary between 2.37 and 2.7 μ_B [33]. The latter values are similar to the values observed for the Fe³⁺ atoms of the presently investigated antimonides. Generally, these higher magnetic moments are understood in terms of spin-orbit coupling [34].

The magnetic properties of the $\text{AFe}_4\text{Sb}_{12}$ compounds

containing magnetic A components may be understood as being composed of both the magnetism of the A component and the magnetism of the $\text{Fe}_4\text{Sb}_{12}$ host lattice. The compound $\text{CeFe}_4\text{Sb}_{12}$ is again paramagnetic with a magnetic moment of $\mu_{\text{exp}} = 2.4 \mu_B$ /f.u., calculated from the slope of the straight line of the $1/\chi$ vs T plot (Fig. 2). For a compound containing only Ce³⁺ or Ce⁴⁺ as carriers of the magnetic moments, the values $\mu_{\text{exp}} = 2.54 \mu_B$ or $\mu_{\text{exp}} = 0 \mu_B$, respectively, would be expected. If Ce⁴⁺ were present, the iron-antimony polyanion is expected electronically to be saturated without a localized magnetic moment. On the other hand, if the cerium atoms were trivalent, both the Ce³⁺ and the $[\text{Fe}_4\text{Sb}_{12}]^{3-}$ polyanion should carry magnetic moments, which together should be greater than the observed value of $\mu_{\text{exp}} = 2.4 \mu_B$. This suggests that the cerium atoms in this compound have a mixed or intermediate valence, and this is indeed also indicated by the reciprocal susceptibility behaviour of $\text{CeFe}_4\text{Sb}_{12}$ below 150 K, which is reminiscent of other mixed or intermediate valent cerium compounds, such as CeSn_3 [35], CeNi [36, 37], CeCu_2Si_2 [38], CeCo_2Ge_2 [39], CeRhSi_2 and CeIrSi_2 [40]. A rough estimate results in a Ce³⁺/Ce⁴⁺ ratio of 40/60. For the isotopic phosphorus compound $\text{CeFe}_4\text{P}_{12}$ a much lower susceptibility was observed [18, 25] and this is in agreement with the higher electronegativity of phosphorus, which favours the higher valence of cerium.

The $1/\chi$ vs T plots of the compounds $\text{PrFe}_4\text{Sb}_{12}$, $\text{NdFe}_4\text{Sb}_{12}$ and $\text{EuFe}_4\text{Sb}_{12}$ indicate ferromagnetism with Curie temperatures of $T_c = 5(2)$ K, $T_c = 13(1)$ K and $T_c = 82(2)$ K. At higher temperatures the $1/\chi$ vs T plots (Fig. 3) suggest Curie-Weiss behaviour. However, the temperature dependence of the reciprocal susceptibility just above the Curie temperatures is not typical for ferromagnets as can be seen best for the compound with the highest Curie temperature, $\text{EuFe}_4\text{Sb}_{12}$. For a simple ferromagnet the $1/\chi$ vs T plot

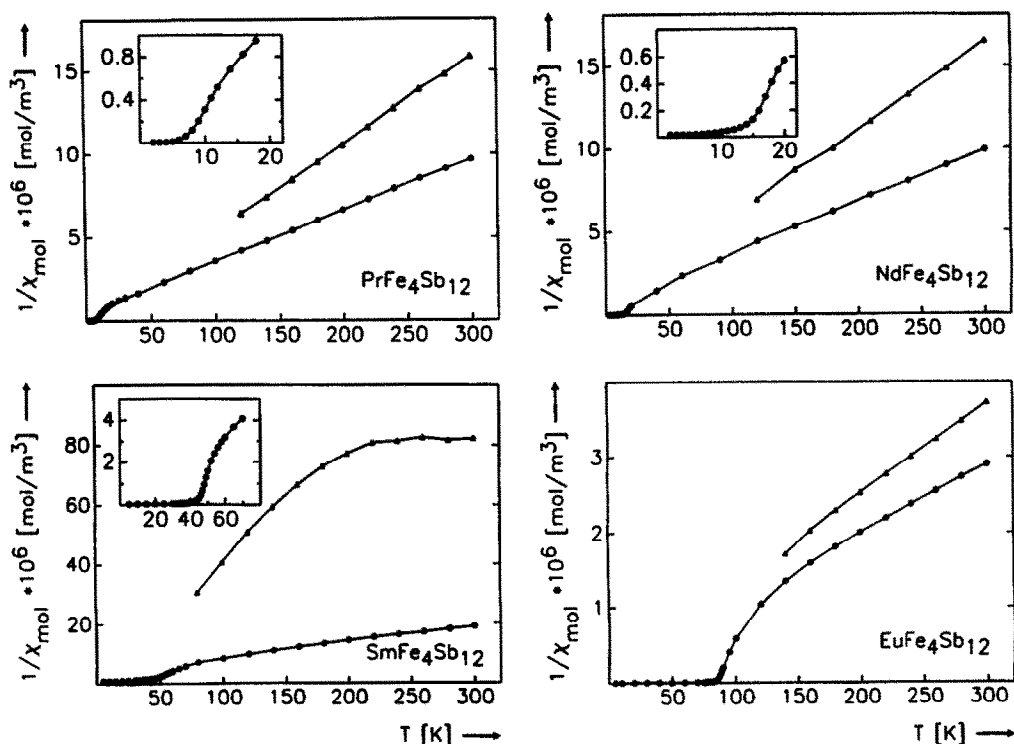


Fig. 3. Reciprocal magnetic susceptibilities χ^{-1} vs temperature of the ternary antimonides $\text{LnFe}_4\text{Sb}_{12}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$ and Eu) measured with a magnetic flux density of 3 T. The insets show the low temperature behaviour in a magnetic field of 0.1 T. Of the two curves in the main diagrams the upper ones indicate the reciprocal susceptibilities obtained from the Ln component after subtracting the susceptibilities of $\text{LaFe}_4\text{Sb}_{12}$ (for the compounds with $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) and $\text{CaFe}_4\text{Sb}_{12}$ ($\text{Ln} = \text{Eu}$) from the total experimental values.

should already be almost linear shortly above the Curie temperature. We attribute the curvature (for $\text{EuFe}_4\text{Sb}_{12}$ between 82 and 140 K) to the interactions of the rare earth moments with the paramagnetic iron–antimony sublattice. Nevertheless, we have evaluated the linear portions of the $1/\chi$ vs T plots according to the Curie–Weiss law. The magnetic moments $\mu_{\text{exp}} = 4.6 \pm 0.2 \mu_{\text{B}}/\text{f.u.}$ and $\mu_{\text{exp}} = 4.5 \pm 0.2 \mu_{\text{B}}/\text{f.u.}$ obtained from these linear portions of the plots for the praseodymium and neodymium compounds, respectively, can be rationalized as consisting of the susceptibilities of both the Ln^{3+} ions and the $[\text{Fe}_4\text{Sb}_{12}]^{3-}$ polyanions. This can be seen from Table 1 by comparing the values of the fifth column $\mu_{\text{exp}}(\text{A})$ with the theoretical values μ_{eff} for the free Ln^{3+} ions, listed in the next column. The values for $\mu_{\text{exp}}(\text{A})$ were calculated from the susceptibilities (as shown in Fig. 3) after subtracting the susceptibilities of $\text{LaFe}_4\text{Sb}_{12}$.

¹⁵¹Eu Mössbauer-spectroscopical investigations of $\text{EuFe}_4\text{Sb}_{12}$ have shown, that the europium atoms in this compound are primarily divalent [41]. Therefore the $\text{Fe}_4\text{Sb}_{12}$ sublattice of this compound is essentially isoelectronic with that of $\text{CaFe}_4\text{Sb}_{12}$. After subtracting the susceptibility of $\text{CaFe}_4\text{Sb}_{12}$ one obtains a magnetic moment of $\mu_{\text{exp}} = 6.8 \pm 0.2 \mu_{\text{B}}/\text{f.u.}$ for $\text{EuFe}_4\text{Sb}_{12}$. This value is below the free-ion moment

for an Eu^{2+} ion, ($\mu_{\text{eff}} = 7.94 \mu_{\text{B}}$), and the difference may be rationalized by a small admixture of Eu^{3+} and/or by the possibility that the europium site is not fully occupied as was already discussed above for the lanthanum and neodymium compounds.

The susceptibility of the samarium compound is temperature dependent in a way frequently observed for the Van Vleck paramagnetic ions Sm^{3+} and Eu^{3+} . After subtracting the contribution of the $\text{Fe}_4\text{Sb}_{12}$ sublattice, the magnetic susceptibility of that compound at room temperature amounts to $\mu_{\text{exp}} = 1.6 \pm 0.2 \mu_{\text{B}}/\text{f.u.}$, which is in good agreement with the paramagnetism of $\mu_{\text{eff}} = 1.66 \mu_{\text{B}}$ calculated from Van Vleck's formula [42] with a screening constant $\sigma = 34$ for 300 K. Below $T_c = 45(2) \text{ K}$, $\text{SmFe}_4\text{Sb}_{12}$ becomes ferromagnetic.

The relatively high magnetic ordering temperatures of these compounds are remarkable, in view of the large interatomic distances of almost 800 pm between the rare earth atoms. This suggests that the magnetic interactions in these metallic compounds occur via the RKKY mechanism. The increase of the Curie temperatures from the praseodymium to the europium compound is in qualitative agreement with the de Gennes function [43]. For the corresponding rare earth iron phosphides the ordering temperatures are

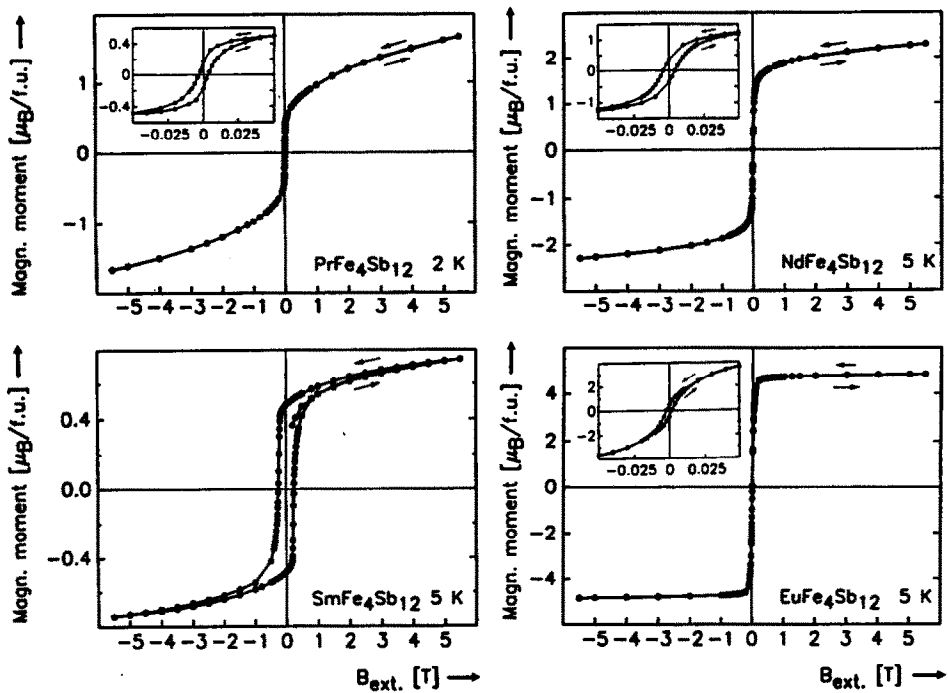


Fig. 4. Hysteresis loops of the four ferromagnetic antimonides $\text{LnFe}_4\text{Sb}_{12}$ determined at temperatures of 2 K ($\text{Ln} = \text{Pr}$) and 5 K ($\text{Ln} = \text{Nd}, \text{Sm}$ and Eu). The insets show the low field magnetisations.

lower [19, 20], with the exception of $\text{EuFe}_4\text{P}_{12}$, which again is ferromagnetic below 100 K [18, 24].

We have investigated the magnetisation behaviour of the ferromagnetic antimonides $\text{PrFe}_4\text{Sb}_{12}$, $\text{NdFe}_4\text{Sb}_{12}$, $\text{SmFe}_4\text{Sb}_{12}$ and $\text{EuFe}_4\text{Sb}_{12}$. The results are shown in Fig. 4 and summarized in Table 2. For the praseodymium compound this investigation was carried out at 2 K, only 3 K below the Curie temperature. This may be the reason why the hysteresis is small and the saturation magnetisation was not reached for the highest magnetic flux density of 5.5 T. For the neodymium compound the saturation magnetisation was nearly achieved. The experimentally determined moment of $\mu_{\text{exp(sm)}} = 2.3 \pm 0.1 \mu_B$ amounts to only 70% of the theoretical value, possibly because this value was obtained from a powder sample with random orientation of the crystallites and furthermore the neodymium site is occupied to only 83.2%, as was already mentioned above.

In contrast, for the samarium compound the magnetisation of $0.7 \mu_B$ achieved with the magnetic flux density of 5.5 T is in good agreement with the theoretical value. With greater magnetic flux densities the saturation magnetisation might even be higher and this could be accounted for by the paramagnetism of the iron–antimony polyanion.

For the europium compound the saturation magnetisation is already reached at low magnetic field strengths and this compound has a very narrow hysteresis loop. Both of these properties may be rationalized with the half filled *f* shell of Eu^{2+} . Again the saturation magnetisation of this compound does not reach the theoretical moment for the reasons already discussed: the presence of a small portion of Eu^{3+} ions, a small percentage of unoccupied sites and the random orientation in a powder sample.

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Table 2. Magnetic characteristics of the ferromagnetic antimonides $\text{AFe}_4\text{Sb}_{12}$ ($\text{A} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$)^a

Compound	$\mu_{\text{exp(sm)}} (\mu_B)$	$\mu_{\text{calc(sm)}} (\mu_B)$	Remanence (μ_B)	H_c (T)	Magnetic behaviour
$\text{PrFe}_4\text{Sb}_{12}$	1.9(1) ^b	3.2 (Pr^{3+})	0.18(1)	0.003(1)	ferromagnetic
$\text{NdFe}_4\text{Sb}_{12}$	2.3(1)	3.27 (Nd^{3+})	0.36(1)	0.004(1)	ferromagnetic
$\text{SmFe}_4\text{Sb}_{12}$	0.7(1)	0.71 (Sm^{3+})	0.48(1)	0.24(1)	ferromagnetic
$\text{EuFe}_4\text{Sb}_{12}$	4.9(1)	7.0 (Eu^{2+})	0.47(1)	0.002(1)	ferromagnetic

^aThe magnetic moments $\mu_{\text{exp(sm)}}$ of the randomly oriented powders obtained from the saturation magnetization at 5 K (for $\text{PrFe}_4\text{Sb}_{12}$ at 2 K) are listed together with the highest possible saturation magnetisation $\mu_{\text{calc(sm)}}$ for optimally oriented moments calculated according to $\mu_{\text{calc(sm)}} = g \cdot J \mu_B$. The remanent magnetisations and the coercivities H_c are also listed.

^bNo saturation at 5.5 T.

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