Ferromagnetic Ordering in Alkali-Metal Iron Antimonides: NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$

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New alkali-metal compounds with the filled-skutterudite structure were synthesized and their chemical and physical properties investigated. X-ray diffraction, microprobe, and chemical analysis established the structure and the composition without defects on the cation site. Magnetization, ac susceptibility, specific heat, resistivity, and NMR or NQR demonstrated NaFe$_4$Sb$_{12}$ to be ferromagnetic below approximately 85 K and to exhibit an additional magnetic anomaly around 40 K. Band structure calculations find a large density of states at the Fermi energy and a ferromagnetic ground state. Similar behavior was observed for KFe$_4$Sb$_{12}$.

Presently, there exists an enormous resurgence of interest in the generic class of compounds known as “skutterudites” [1,2]. These materials derive from the ternary structure NaFe$_4$Sb$_{12}$ (space group $Ia3d$), and can be synthesized with the general formula $MT_4X_8$, where $M$ is a rare-earth or an alkaline-earth metal, $T$ is a transition metal of the iron or cobalt group, and $X$ is a pnictide (P, As, or Sb) [3]. Recently, a plethora of topical behaviors has been observed with various rare-earth elements ranging from metal-insulator transitions to magnetic and quadrupole orderings, unconventional superconductivity, heavy fermion/non-Fermi liquids, and fluctuating/mixed valency [4,5]. Here, combinations of these effects can be tuned to coexist and interact. Another reason for the popularity of this family is its possible use in thermoelectric applications due to the low electric resistivity and large thermal power and resistivity [6].

Despite these intense efforts a number of fundamental properties remain unknown, as, for example, the relationship and interplay between the rare-earth and the transition metal [7]. Interestingly, for $T = Fe$ the binaries Fe$_4X_8$ seem not to be stable under equilibrium conditions [8] and only filled variants are stable. Nevertheless, attention is usually focused on and dominated by the specific rare-earth element whose $f$ electrons generate the above mentioned behaviors and less notice is taken of the $T$ species and its contribution to the skutterudite physics.

In order to circumvent this ambiguity and to explore novel classes of non-rare-earth skutterudites, we successfully synthesized alkali-metal compounds. Now the “cage filler” is a light mass, single $s$-electron metal that is not magnetic or superconducting and contributes only marginally to the states of the valence band. When combined with $T = Fe$, we observe the unexpected appearance of long-range ferromagnetic order with rather small ordered moments at $T_c \approx 85$ K enmeshed in a spectrum of strong spin fluctuations. The low ratio of the ordered moment and $T_c$ sets the new compounds clearly apart from the known rare-earth filled skutterudites. In fact, it is the first observation of magnetic ordering at the $T$ sublattice in skutterudites. In this Letter, we examine the basic structural properties of NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ through x-ray diffraction (XRD), electron probe microanalysis (EPMA), and chemical analysis. The physical properties were determined through bulk thermodynamic and transport measurements and by using nuclear resonance methods ($^{23}$Na NMR and $^{121,123}$Sb NQR) as local probes. The experimental data are supported by results of full-potential band structure calculations using the local spin density approximation (LSDA).

Because of the high vapor pressure of the alkali metals polycrystalline samples of NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ were prepared in a two step synthesis. First, the binary compounds NaSb and KSb were synthesized. Then, a stoichiometric mixture of powdered monoantimonides together with FeSb$_2$ and Sb was reacted at 400 $^\circ$C for one week. Since binary alkali-metal antimony compounds are very sensitive to air the preparation was carried out in an Ar-atmosphere glove box system (oxygen and water less than 1 ppm). The ternary compounds were obtained as dark grey powders. In contrast to the binaries, they are relatively stable against air and moisture.

Physical property measurements were performed on specimens cut from compacted samples which were prepared by spark plasma sintering (SPS) the powders at 200 $^\circ$C. Sample densities of 80% of the theoretical value could be achieved. Metallographic and EPMA investigation of polished specimens revealed elementary antimony as the only impurity phase present (less than 0.5 vol %).

Powder XRD data gave cubic (space group $Im3$) lattice parameters $a = 9.1767(5)$ Å for NaFe$_4$Sb$_{12}$ and $a = 9.1994(5)$ Å for KFe$_4$Sb$_{12}$, respectively. Chemical analysis together with EPMA confirmed the stoichiometric composition. No indications of a defect occupation of the cation position were found. Single crystal XRD analysis of NaFe$_4$Sb$_{12}$ corroborated the full occupancy of the...
Na 2α position inside the distorted icosahedral cages in the antimony-iron framework in full accordance with a filled-skutterudite structure of the LaFe₄P₁₂ type [3,9]. Iron atoms are located on an 8c position, Sb on a 24g site. Sodium shows a large thermal displacement parameter ($U_{Na} = 5U_{Fe} = 4U_{Sb}$) suggesting a “rattling” motion or static displacement inside the cavity. Thermal expansion of NaFe₄Sb₁₂ was studied by low temperature powder XRD in the range from 15 to 300 K. A volume expansion of $\Delta V / V(15 K) = 0.71\%$ was observed in this temperature range; however, no indications for structural transitions were detected [9].

The field cooling (fc) and zero field cooling (zfc) magnetization curves were measured. The new alkali-metal compounds NaFe₄Sb₁₂ (Fig. 1) and KFe₄Sb₁₂ were found to order ferromagnetically at $T_C = 85$ K. For a sample of NaFe₄Sb₁₂ (SPS treated) the remanent moment at 1.8 K is 0.28 $\mu_B$ per Fe atom (Fig. 1 inset). The magnetization increases smoothly to 0.60 $\mu_B$ in an external field of 14 T (not shown). Similar magnetization values are found for noncompacted NaFe₄Sb₁₂ and KFe₄Sb₁₂ samples. In the paramagnetic range an effective magnetic moment per Fe atom of 1.6–1.8 $\mu_B$ can be extracted by a fit with a Curie-Weiss law for the two alkali-metal as well as for the Ba and Ca compounds. The paramagnetic Weiss temperature $\Theta$ is positive and nearly identical with $T_C$ for the alkali compounds. For BaFe₄Sb₁₂, which we use as a reference compound, the ferromagnetic interactions are much weaker ($\Theta = +10–25$ K), while they are remarkably strong for CaFe₄Sb₁₂ ($\Theta = +45$ K). No bulk magnetic ordering down to 2 K was detected for the Ca and Ba compounds; however, an upturn of the fc susceptibility for low external fields and a much smaller zfc signal may indicate precursor effects of ferromagnetic ordering below approximately 20 K. All these findings indicate that a bulk ferromagnetic state exists only for the alkali-metal filled compounds.

For the Na and K compounds a sharp peak was observed at $T_C = 85$ K in the real part ($\chi'$) of the ac susceptibility (Fig. 2). Around 40 K a strongly frequency-dependent maximum emerged in the imaginary part ($\chi''$). This indicates a glasslike dynamical change in the magnetic state at this temperature well below $T_C$.

The electrical resistivities $\rho(T)$ (not shown) of the Na, K, Ba, and Ca compounds are nevertheless similar: the $\rho(T)$ curves increase in an “S” shape up to roughly 150 K above which they increase linearly. $\rho(300 K) \approx 1500 \mu\Omega\text{cm}$ and thus the materials can be classified as “bad” metals. For the Na and K compounds tiny peaks are visible in $\rho(T)$ at $T_C$. Below 20 K we find $\rho - \rho_0 = AT^2$ with $A = 1.780 \times 10^{-9}$ (Na) and $1.207 \times 10^{-9} \Omega\text{mK}^{-2}$ (K).

Heat capacity measurements were performed on NaFe₄Sb₁₂ and BaFe₄Sb₁₂ for 1.8 K $< T < 300$ K using a relaxation method. The results confirm the existence of bulk ferromagnetism with a $T_C = 85$ K for NaFe₄Sb₁₂, whereas for BaFe₄Sb₁₂ no signs of magnetic order are observed (see Fig. 3). As a first approach we use BaFe₄Sb₁₂ to estimate the magnetic contribution to the specific heat $c_m(T)$ of NaFe₄Sb₁₂. Besides the phase transition at 85 K, $c_m(T)$ shows an additional anomalous contribution around 30 K (see Fig. 3 inset), which is probably magnetic in origin. Similar evidence comes from above mentioned ac-susceptibility ($\chi''$) data.

Staying with zero field values [10], for NaFe₄Sb₁₂, the linear electronic coefficient $\gamma$ obtained for $T < 14$ K is large (145 mJ mol⁻¹ K⁻²). This yields a value of 62 states eV⁻¹ f.u⁻¹ (f.u. = formula unit) for the total density of states at the Fermi level, $N(E_F)$. For BaFe₄Sb₁₂ the value of 115 mJ mol⁻¹ K⁻² corresponding to $N(E_F) = 50$ states eV⁻¹ f.u⁻¹ is found. For both ferromagnetic compounds the ratio $A / \gamma^2$...
from 4.2 to 290 K. The spin-lattice relaxation rate \( \frac{1}{\tau} \) of \( \text{NaFe}_4\text{Sb}_{12} \) was found at 290 K. The isotropic Knight shift was obtained by relaxation-recovery techniques. In absolute value the system becomes more magnetic and the magnetic interaction at the sodium site. With decreasing temperature the system becomes more magnetic and the absolute value \(|K|\) becomes larger. \(|K(T)|\) shows the same overall behavior as the \( T \) susceptibility. From the analysis of the \( K(\chi) \) plot (see Fig. 4), we could obtain two distinct hyperfine coupling constants \( A_s, A_s^1 = -14.49 \text{ kOe} / \mu_B \) above \( T_C \) and \( A_s^2 = -11.55 \text{ kOe} / \mu_B \) below \( T_C \) in the ferromagnetic phase using the equation for a pure \( s \) orbital \( (A_s = N_s \mu_B dK/d\chi_s) \). These relatively low values \( A_s \) are in agreement with the small ordered magnetic moments of iron observed in both dc-magnetization experiments and local spin density approximation calculations (see below).

The plot of \( 1/T_1(T) \) (Fig. 4 inset) shows linear dependence in the ferromagnetic region for \( T \to 0 \), thus obeying the Korringa relation [10] with a small anomaly between 30 and 40 K. The linear behavior is consistent with the results for \( |K| \) in the framework of Korringa theory, and \( c_p(T) \) and \( \chi_M \) show similar features around 40 K. After a dip at \( T_C \) \( 1/T_1 \) increases sharply in the paramagnetic state and becomes nearly constant around 160 K. This behavior is unusual, because for ferromagnets one expects a peak in \( 1/T_1 \) close to \( T_C \) usually attributed to strong spin fluctuations near \( T_C \) [11].

The antimony NQR spectrum (not shown) consists of five lines which are assigned to two transition lines for \( ^{123}\text{Sb} (S = 5/2) \) and three lines for \( ^{125}\text{Sb} (S = 7/2) \). This assignment confirms the existence of only one crystallographic site according to the structure. Below \( T_C \) all lines decrease sharply to zero demonstrating the onset of the ferromagnetic ordering through an increase of the internal field at the antimony site.

A full-potential nonorthogonal local-orbital scheme [12] within the LSDA was used to obtain accurate electronic structure information. In the scalar relativistic calculations we used the exchange and correlation potential of Perdew and Wang [13]. \( \text{Na} (2s, 2p, 3s, 3p, 3d), \text{Fe} (3s, 3p, 4s, 4p, 3d), \text{and Sb} (4s, 4p, 4d, 5s, 5p, 5d) \) states, respectively, were chosen as the basis set. All lower lying states were treated as core states. The \( \text{Na} 3d \) states as well as the \( \text{Sb} 5d \) states were taken into account to increase the completeness of the basis set. The inclusion of the \( \text{Na} (2s, 2p), \text{Fe} (3s, 3p), \) and \( \text{Sb} (4s, 4p, 4d) \) states in the valence states was necessary to account for non-negligible core-core overlaps. The spatial extension of the basis orbitals, controlled by a confining potential [14] \((r/r_0)^{18}\), was optimized to minimize the total energy. A \( k \) mesh of 396 points in the irreducible part of the Brillouin zone was used.

The calculation results in a valence band of about 5 eV band width, formed mainly by \( \text{Fe} 3d \) and \( \text{Sb} 5p \) states (see Fig. 5). The density of states at the Fermi level is high with about 42 states eV\(^{-1}\)f.u.\(^{-1}\). In a spin polarized calculation, we find a ferromagnetic ground state with a total moment of 2.97\( \mu_B \) per cell. The main contribution comes from \( \text{Fe} (0.82\mu_B \text{ per atom}) \), while \( \text{Sb} \) (-0.02\( \mu_B \)) and \( \text{Na} \) (-0.05\( \mu_B \)) show slightly opposite spin polarization. Assigning magnetic moments to the Fe sites only, this results in 0.74\( \mu_B \) per Fe atom. The total energy of the ferromagnetic solution is lower by 0.236 eV/f.u. than that of the paramagnetic state.

To look for possible origins of magnetic anomalies, we have calculated the energy-versus-moment curve by fixed

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**FIG. 3** (color online). Specific heat capacity of \( \text{NaFe}_4\text{Sb}_{12} \) and \( \text{BaFe}_4\text{Sb}_{12} \) vs temperature. (a) Magnetic contribution plotted as \( c_m/T \) vs \( T \). (b) \( c_p/T \) vs \( T^2 \) at low temperatures.

**FIG. 4** (color online). Knight shift of \( ^{23}\text{Na} \) vs dc susceptibility \( \chi(T) \) with temperature as the implicit parameter for \( \text{NaFe}_4\text{Sb}_{12} \). The inset shows inverse spin-lattice relaxation times \( 1/\tau_1 \) vs \( T \).
Below 85 K with a low saturation moment for both filled-skutterudite structure. Itinerant ferromagnetism characterized two new alkali-metal iron antimonides with the NaFe$_4$Sb$_{12}$ respectively \[15\]. The increase of the magnetic moment in treatments. The small ratio of ordered moment and measurements. These results are consistent with LSDA calculations.

The size of the LSDA moment overestimates the experimental zero field moment of about 0.3$\mu_B$ considerably. A possible explanation could be the reduction of the ordered moment by strong spin fluctuations not included in the framework of LSDA. The basic theoretical difficulty in correcting LSDA results for this type of material is the separation of this nonincluded quantum-critical fluctuations from the dynamical fluctuations that are included \[15\]. A similar behavior is observed in ZrZn$_2$, in Na$_3$Al, or in FeAl, where critical fluctuations reduce the moment strongly or even prevent magnetic ordering at all, respectively \[15\]. The increase of the magnetic moment in NaFe$_4$Sb$_{12}$ to 0.60$\mu_B$ (0.65$\mu_B$ extrapolating to $1/H \to 0$) when suppressing critical fluctuations in a field of 14 T would be consistent with this explanation.

In conclusion, we have synthesized and fully characterized two new alkali-metal iron antimonides with the filled-skutterudite structure. Itinerant ferromagnetism below 85 K with a low saturation moment for both NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ was established via a variety of thermodynamic and magnetic resonance measurements. These results are consistent with LSDA calculations. The small ratio of ordered moment and $T_C$ as well as the site of the moments imply a completely different type of magnetic interactions compared to the rare-earth containing skutterudites. Experiments and calculations in order to determine the relationship between the appearance of ferromagnetism in the alkali compounds and the unique chemical bonding in filled-skutterudite structure compounds are presently under way. Inspecting the electronic density of states already gives strong indication of significant hybridization of Fe 3$d$ and Sb 5$p$ states. As evidenced by a preliminary analysis of chemical bonding by electron localization function calculations \[9\], the Fe-Sb framework forms a unique rigid covalently bonded polyanion. Since the binary FeSb$_3$ is metastable \[8\], the polyanion is stabilized by a charge transfer from the filler ion. The amount of charge transferred can be considered a coordinate on which the various electronic ground states of skutterudites occur. In addition, $d$-element spin fluctuations and $f - d$ electron hybridization play an important role.

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