

Alkaline-Metal-Iron Antimonides $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$ with the filled Skutterudite Structure of $\text{LaFe}_4\text{P}_{12}$ Type.

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The mineral Skutterudite CoAs_3 is the archetypal compound for the entire family of isostructural materials often called “skutterudites”. The skutterudite-like isostructural compounds MPn_3 ($M = \text{Co, Rh, Ir, Pn} = \text{P, As, Sb}$) were investigated intensively as potentially good thermoelectric materials [1,2].

The body centered cubic crystal structure (space group $Im\bar{3}$) is composed of a 3D network formed by 24 pnictogen atoms giving rise to the formation of different voids in the crystal structure. The octahedral voids are occupied by transition metal atoms. Taking into account that one unit cell contains two formula units the stoichiometric composition can be expressed as $M_8[\text{Pn}_4]_6$. Due to the concerted tilting of each of the four octahedra, pnictogen atoms at the corners come into close contact, thus forming planar rectangular rings. In this structural arrangement no direct contacts between the transition metal atoms do exist. The binary compounds are diamagnetic semiconductors which correspond to a closed shell configuration in a chemical bonding sense. No binary pnictogen compound of the iron group does exist with the skutterudite type of structure.

Parts of the cavities inside the pnictogen substructure (with the center at the origin) are of sufficient size to accommodate guest atoms (Fig. 1). The composition of the unit cell would be $[\text{}]_2M_8[\text{Pn}_4]_6$. This situation can be realized by switching from the 9th (cobalt) group to the 8th (iron) group of periodic table and allows alloying of more electropositive metals as a third component [3]. The cation which resides in the voids may be a lanthanide (RE), actinide, alkaline-earth (AE) or – as shown in this contribution – an alkaline metal. In a first approximation this experimental facts can be understood by considering a donation of electrons from the cations to the transition-metal-pnictogen substructure which (for iron-group metals) is deficient in electrons compared to that observed in the binary phases of the group 9 metals.

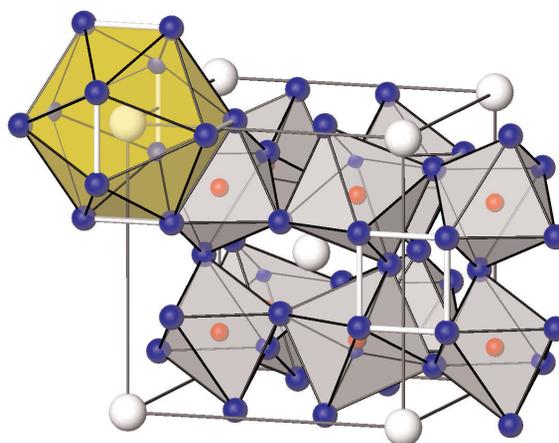


Fig. 1: The crystal structure of $\text{NaFe}_4\text{Sb}_{12}$. White spheres: Na, blue: Sb and red: Fe. Close Sb-Sb contacts ($d = 2.9145 \text{ \AA}, 2.9944 \text{ \AA}$) are indicated by bold white lines.

Due to a complex interplay of the parent transition-metal-pnictogen-network with the cations, these ternary compounds exhibit a wide range of physical properties such as heavy-fermion behavior ($\text{CeFe}_4\text{Sb}_{12}$ and $\text{PrFe}_4\text{Sb}_{12}$) and additional superconductivity ($\text{PrOs}_4\text{Sb}_{12}$ [1], see also “*B-T Phase Diagram of $\text{PrOs}_4\text{Sb}_{12}$...*”). The interest in those materials is currently stimulated by promising prospects of application as thermoelectric materials. The relatively high thermoelectric figure of merit has been correlated with the influence of the cations on the lattice thermal conductivity [1,2,4].

Here we focus on the alkaline metal iron antimonides $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$ which crystallize in the filled skutterudite structure type $\text{LaFe}_4\text{P}_{12}$ (FSS) [3]. Alkaline metals were chosen in order to study the magnetic properties of iron in the antimony framework without the complicating influence of f -electron bearing species. Furthermore ^{23}Na and $^{121,123}\text{Sb}$ are excellent nuclei for magnetic resonance spectroscopy, thus being a local probe for analyzing the chemical and magnetic influences of the host structure on the atom localized in the icosahedral void.

The compounds $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$ were obtained as polycrystalline material. Powder XRD data give cubic lattice parameters $a = 9.1767(5)$ Å for $\text{NaFe}_4\text{Sb}_{12}$ and $a = 9.1994(5)$ Å for $\text{KFe}_4\text{Sb}_{12}$, respectively. Chemical analysis together with electron probe microanalysis confirmed the partial composition. No indications of a defect occupation of the cation position were found. Single crystal XRD analysis of $\text{NaFe}_4\text{Sb}_{12}$ corroborates the full occupancy of the Na $2a$ position inside the distorted icosahedral cages formed by the antimony-iron framework (see Fig. 1).

Iron atoms are located on an $8c$ position, Sb on a $24g$ site. Sodium shows a large thermal displacement parameter suggesting a “rattling” motion inside the cavity.

Ferromagnetic order at surprisingly high temperatures – in spite of the large distance between the cations – was reported for the magnetic moments of various rare-earth metals in $\text{REFe}_4\text{Sb}_{12}$ compounds [5]. The magnetic moments of the iron sublattice does not order in $\text{REFe}_4\text{Sb}_{12}$ and in $\text{AEFe}_4\text{Sb}_{12}$ with $\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$ [5]. These materials remain paramagnetic down to 2 K, but some interesting field-dependent effects are observed in the magnetization of $\text{BaFe}_4\text{Sb}_{12}$ below 50 K, which might originate from ferromagnetic correlations. In contrast, our new alkali-metal compounds $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$ were found to order ferromagnetically at $T_C \approx 85$ K (Fig. 2). For a sample of $\text{NaFe}_4\text{Sb}_{12}$ compacted by spark plasma sintering (SPS) the remanent saturation moment (per f.u.) at 1.8 K is $1.12\mu_B$ (Fig. 2 inset). The magnetization increases smoothly to $2.4 \mu_B$ in an external field of

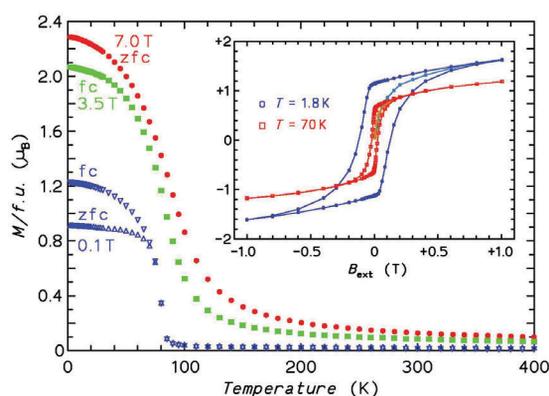


Fig. 2: Magnetization of an SPS compacted sample of $\text{NaFe}_4\text{Sb}_{12}$. Red- 7T zfc; green-3.5 T zfc; blue-0.1 T zfc/zfc. Inset: isothermal hysteresis loops at 1.8 K and slightly below T_C (70 K).

14 T. Similar magnetization values are found for more porous samples and for $\text{KFe}_4\text{Sb}_{12}$. In the paramagnetic range an effective magnetic moment per Fe atom of $1.6 \mu_B - 1.8 \mu_B$ can be deduced from a fit with a Curie-Weiss law for both alkali-metal as well as for the Ba compounds. The paramagnetic Weiss temperature Θ is positive and nearly identical with T_C . For $\text{BaFe}_4\text{Sb}_{12}$ the ferromagnetic interactions are much weaker ($\Theta = +10\text{K}$) and no ordering was detected down to 2 K. All these findings indicate, that a bulk ferromagnetic state exists only for the alkali-metal FSS compounds.

The electrical resistivity curves $\rho(T)$ of the Na, K and Ba compounds are nevertheless very similar: $\rho(T)$ increases with an “S” shape up to ca. 150 K above which it increases linearly. $\rho(300 \text{ K})$ is about $1500 \mu\Omega\text{cm}$. At the Curie temperatures tiny peaks due to critical effects near the phase transition are visible. No significant spin-disorder contribution to the resistivity is found.

Heat capacity measurements were performed on compounds $\text{NaFe}_4\text{Sb}_{12}$ and $\text{BaFe}_4\text{Sb}_{12}$ in the temperature range 1.8 K to 300 K using a relaxation method. The results confirm the existence of bulk ferromagnetism with a $T_C \approx 85$ K for $\text{NaFe}_4\text{Sb}_{12}$, whereas for $\text{BaFe}_4\text{Sb}_{12}$ no signs of magnetic order are observed (see Fig. 3). As a first approach we use $\text{BaFe}_4\text{Sb}_{12}$ as a phonon reference and estimate the magnetic contribution to the specific heat $c_m(T)$ of $\text{NaFe}_4\text{Sb}_{12}$.

Besides the phase transition at 85 K, $c_m(T)$ shows an additional anomalous contribution around 30 K (see inset Fig. 3a), which is probably magnetic in origin. This evidence comes from the ac magnetic

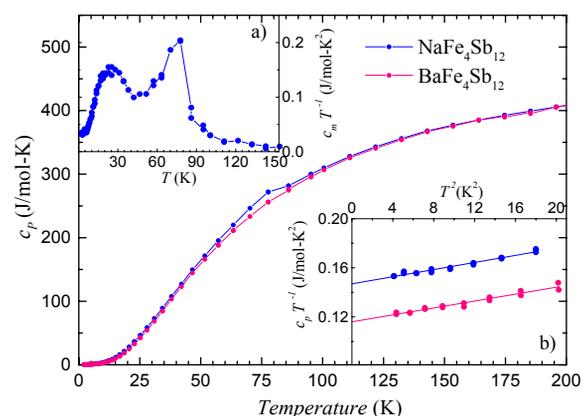


Fig. 3: Specific heat c_p of $\text{NaFe}_4\text{Sb}_{12}$ and $\text{BaFe}_4\text{Sb}_{12}$ vs. temperature. Inset a: c_m/T vs. T . Inset b: c_m/T vs. T^2 .

susceptibility measurements which show a peak in the imaginary part χ'' at ~ 40 K. Anomalous behavior in this temperature range is also confirmed by the ^{23}Na NMR investigations (see below). It could be speculated that this anomaly is a consequence of a charge redistribution driven by a “lock-in” transition of the Na “rattlers”. The spin wave contribution to $c_p(T)$ in the ferromagnetically ordered state ($\propto T^{3/2}$) seems to be less important at low temperatures. In the case of $\text{NaFe}_4\text{Sb}_{12}$, γ is large ($145 \text{ mJ mol}^{-1}\text{K}^{-2}$). This yields a value of $62 \text{ eV}^{-1}\text{f.u.}^{-1}$ for the total density of states at the Fermi level, $N_\gamma(E_F)$, which is much larger than the density of states value $N_{\text{BS}}(E_F)$ ($20.98 \text{ eV}^{-1}\text{f.u.}^{-1}$) obtained from the band structure calculations using the LMTO method. For $\text{BaFe}_4\text{Sb}_{12}$ the value of $\gamma \sim 115 \text{ mJ mol}^{-1}\text{K}^{-2}$ corresponding to $N_\gamma(E_F) 50 \text{ eV}^{-1}\text{f.u.}^{-1}$ ($N_{\text{BS}}(E_F) = 30 \text{ eV}^{-1}\text{f.u.}^{-1}$). For both the compounds, $N_\gamma(E_F)$ is higher than $N_{\text{BS}}(E_F)$. Since the band structure calculations do not take into account the effects of strong electronic correlations, the density of states is expected to be underestimated.

$\text{NaFe}_4\text{Sb}_{12}$ was investigated by means of ^{23}Na (nuclear spin $I = 3/2$) NMR in the temperature range from 4 K to 290 K. With MAS (magic angle spinning) NMR experiments at 300 K (diluted sample with boron nitride) only one sodium position could be detected in agreement with structural investigations. The isotropic Knight shift $K = -0.128(7) \%$ points to weak paramagnetic interactions at the sodium site. Due to the distorted icosahedral antimony surrounding of sodium ($d(\text{Na-Sb}) = 3.4175 \text{ \AA}$) a small anisotropy of about 272 ppm (21.6 kHz) was observed.

This can be explained by small first order quadrupolar interactions together with an anisotropy of the Knight shift. Second order quadrupolar interactions do not occur. The asymmetry parameter $\eta = 0.95$ is close to one which reflects asymmetric interactions with the electric field gradient. Knight shift as a function of temperature shows a similar behavior as the susceptibility. It is negative with an increasing magnitude for decreasing temperature. Below T_C the ferromagnetic state strongly effects the Knight shift. The connection between K and spin susceptibility $\chi_\alpha^{\text{spin}}$ is expressed as $K_\alpha^{\text{spin}} = A_\alpha \chi_\alpha^{\text{spin}}$. Using that equation the total hyperfine coupling constant A_α can be calculated. $A_\alpha = A_\alpha^{\text{Fermi}} + A_\alpha^{\text{dip}} + A_\alpha^{\text{so}}$, where the contributions are the Fermi contact, dipole, and spin-orbit hyperfine coupling constants, respectively.

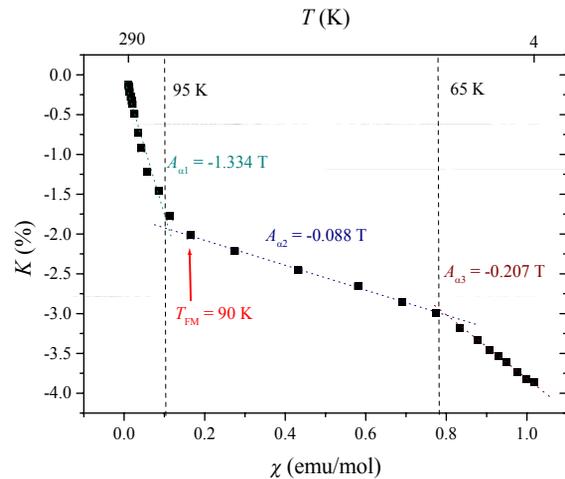


Fig. 4: Knight shift K vs. susceptibility χ over the temperature range from 4 K to 290 K observed for $\text{NaFe}_4\text{Sb}_{12}$ ($B_0 = 7T$).

In the present case, the dipolar and spin-orbit contributions vanish for a pure s -orbital. Therefore, A_α is equal to A_α^{Fermi} and is determined by $A_\alpha = N_{\text{A}\mu\text{B}} dK/d\chi_\alpha$. From a K versus χ plot three different linear regimes corresponding to three different hyperfine coupling values were observed (Fig. 4). The values of the calculated hyperfine coupling constants are: $A_{\alpha 1} = -1.334 \text{ T}$, $A_{\alpha 2} = -0.088 \text{ T}$, and $A_{\alpha 3} = -0.207 \text{ T}$. The relatively small hyperfine couplings are in agreement with the small ordered magnetic moments (attributed to iron) found in the magnetization measurements.

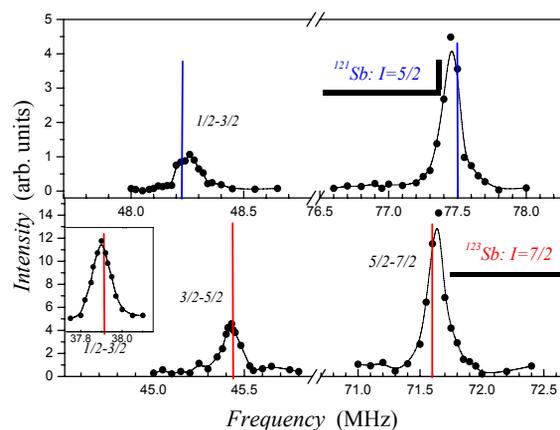


Fig. 5: $^{121,123}\text{Sb}$ NQR spectrum at $T = 300 \text{ K}$. Solid lines are the exact solution of quadrupole Hamiltonian for $I = 5/2$ and $I = 7/2$ with $\eta = 0.45$.

Spin-lattice relaxation experiments are currently under way to obtain more information about the dynamics i.e. (the “rattling” of the sodium atom in the antimony cage) and/or magnetic effects below T_C . The antimony NQR spectrum measured at 300 K consists of five lines which are assigned to two NQR transition lines for the ^{121}Sb ($I = 5/2$) and three lines for ^{123}Sb ($I = 7/2$) isotopes with $\eta = 0.45$ (see Fig. 5). This assignment confirms the existence of only one crystallographic site in the antimony framework with essentially non-axial symmetry. The intensities of all NQR lines sharply decrease to zero below 90 K indicating a magnetically ordered state.

References

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