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^{23}Na NMR investigations of the itinerant ferromagnets $NaFe_4Sb_{12}$ and $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$

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Abstract

A ^{23}Na ($I = \frac{3}{2}$) NMR study is presented on the itinerant ferromagnets $NaFe_4Sb_{12}$ and the isostructural Ca-substituted compound $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ performed in 7.05 and 11.74 T in the temperature range from 4 to 300 K. Both compounds show a bulk ferromagnetism below 85 K. Static (Knight-shift) and dynamic (spin-lattice relaxation) measurements are described in the framework of the SCR theory for itinerant d band metals.

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1. Introduction and experimental

Research on filled skutterudites MT_4X_{12} (T = Fe, Ru, Os; X = P, As, Sb) is mainly focussed on rare-earth systems due to the occurrence of strong correlations leading to superconductivity, heavy-Fermion or Kondo insulator behaviour [1–4]. In contrast, our investigations are devoted to the new systems MFe_4Sb_{12}, with M = Na, K, Ca or Ba, where the magnetism comes exclusively from iron. $NaFe_4Sb_{12}$ and KFe_4Sb_{12} show bulk ferromagnetism below 85 K, whereas the Ca and Ba compounds are not. Fixed moment calculations suggest that strong spin-fluctuations prevent ferromagnetic order in the Ca and Ba systems. $NaFe_4Sb_{12}$ and also the 50% Ca-substituted compound, $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ exhibit surprisingly the same ferromagnetic ordering temperature accompanied by weak itinerant iron moments and critical spin-fluctuations [5–8]. Both compounds crystallize in a BCC crystal structure.

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($Im\,\bar{3}$). It is suggested that $NaFe_4Sb_{12}$ belongs to the class of half-metallic ferromagnets which are promising materials for spin-electronic devices [6,9]. ^{23}Na NMR investigations on the Ca-substituted sample in comparison with the pure sample provide new information about the magnetism and its development on a microscopic scale.

The ^{23}Na NMR spectra were obtained using a Bruker MSL 300 spectrometer ($B_0 = 7.05\,T$) and a Bruker Avance 500 ($B_0 = 11.74\,T$) spectrometer. A spin-echo pulse sequence ($90^\circ - \tau - 180^\circ$) was employed. The ^{23}Na spin-lattice relaxation times were measured with the saturation-recovery technique. The Knight-shifts were estimated with a 1 M NaCl solution ($K_{NaCl} = 0.00\%$) as reference.

2. Results and discussion

The ^{23}Na Knight-shift (K) as a function of temperature is plotted in Fig. 1 together with the DC-susceptibility (χ) (see inset). $K(T)$ is nearly equal for the pure and the Ca-substituted sample, whereas differences in the $\chi(T)$ plot appear especially at lower temperatures. K is negative over the entire temperature range which indicates a dominant indirect transferred interaction via core polarization of the inner Na shells due to itinerant 3d iron electrons [10–12].

The hyperfine coupling constant A_{hf} is given by $N_A \mu_B \mathrm{d}K/\mathrm{d}\chi$. Two different hyperfine coupling constants were calculated for each compound from the two linear regimes above and below T_C (Fig. 2). In general both, K and χ as well are composed of contributions from d spins (transferred field), s-like conduction electrons (Fermi contact field), and diamagnetic core contributions. The intercept points with the K axis (for $\chi \to 0$) provide rough estimations of the diamagnetic and s-conduction electron contributions. These values are negligibly small ($K_0 = +0.19\%$ for $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ and $K_0 = +0.15\%$ for $NaFe_4Sb_{12}$). The larger value for the Ca-substituted compound is suggested from band structure calculations which indicate a higher DOS as for $NaFe_4Sb_{12}$ due to the larger carrier concentration.

$1/T_1$ depends strongly on the external field. Critical spin-fluctuations are dominant in lower fields (3.5 T) [7] while a clear kink is observed at higher fields (7.05 T, 11.74 T). Moriya's SCR theory: $1/T_1 = T\chi k/(1 + \chi^3 B^2 a_F)$ [11] gives a sufficient agreement between data and calculations (Fig. 3). For the description of $1/T_1(T)$ data a set of two a_F and one k parameters are required. The a_F parameter is related to the Fermi surface of the 3d electrons. The kink indicates the crossover from a larger to a smaller Fermi surface as evidenced from band structure calculations.

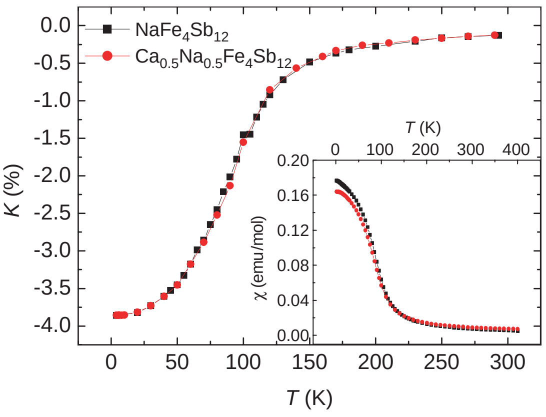

Fig 1. K vs. T, inset χ vs. T, of $NaFe_4Sb_{12}$ and $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ in $B_0 = 7.05\,T$.

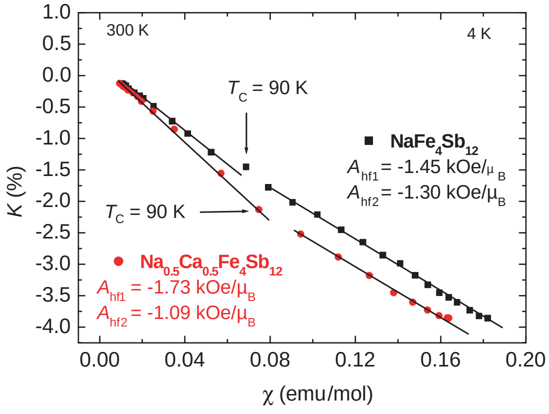

Fig. 2. K over χ of $NaFe_4Sb_{12}$ and $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ in $B_0 = 7.05\,T$.

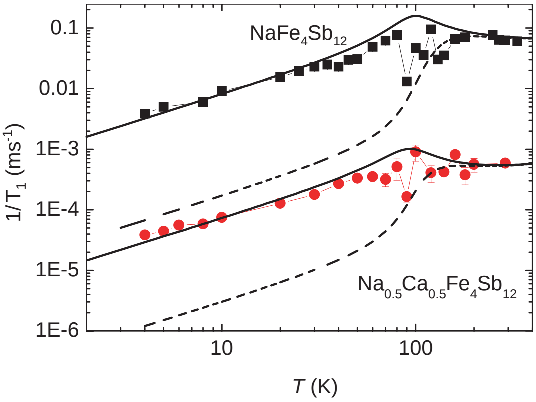

Fig. 3. $1/T_1(T)$ of $NaFe_4Sb_{12}$ and $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$ in $B_0 = 7.05\,T$ with the appropriate Moriya calculations (for small a_F: solid line and for large a_{F0}: dashed line, $NaFe_4Sb_{12}$: $a_F = 0.01\,a_{F0}$ and $Na_{0.5}Ca_{0.5}Fe_4Sb_{12}$: $a_F = 0.03\,a_{F0}$).

3. Conclusions

From ^{23}Na NMR investigations, we determined that the nature of the ferromagnetism is robust against Ca-substitution. $K(T)$ is very similar for both samples, where the A_{hf} values are surprisingly small, negative, and slightly different. We attribute this to small itinerant magnetic moments and weak core polarization.

T_1 is nicely described within the SCR theory with a clear sign for reduction of the d-electron Fermi surface ($\sim a_F$) at T_C. The difference in a_F is smaller for the Ca-substituted sample ($a_F = 0.03\,a_{F0}$) which indicates a slightly larger Fermi surface.

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