High field Mössbauer study of $REFe_4Sb_{12}$ skutterudites

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Abstract

The partly filled skutterudites $RE_xFe_4Sb_{12}$ (RE = La, Pr, Nd, Eu, and Yb) were investigated at 4.2 K by ^{57}Fe Mössbauer spectroscopy in external fields up to 13.5 T. In accordance with the filling factor determined by X-ray investigations two Fe sites were identified, favoring a statistical distribution of voids and RE atoms on the 2*a* lattice positions. For all investigated compounds the values of the induced hyperfine fields are much too small to explain directly the large effective moments deduced on the Fe sites from susceptibility measurements at high temperatures.

Introduction

Investigations of the ground state properties of ternary, partly filled skutterudites $RE_xFe_4Sb_{12}$ are of significant importance to exploit their high thermoelectric potential for future applications. The RE atoms are situated in oversized cages and influence by anharmonic vibrations the thermal conductivity [1, 2]. Changes of the number of voids in the RE sublattice offer thus the possibility to tailor the thermoelectric figure of merit.

In spite of the large amount of theoretical and experimental investigations performed on these compounds, precise knowledge about the magnetic moment on the Fe atoms is still missing [e.g. 1 and references herein]. To obtain experimental evidence of these moments and in addition a more detailed knowledge about the magnetic ground state, we started with high field Mössbauer measurements on compounds with RE = La, Pr, Nd, Eu, and Yb.

$LaFe_4Sb_{12}$ is nonmagnetic, at least down to 2 K with μ_{eff} = 3.0 μ_B/fu derived from susceptibility measurements at higher temperatures [3]. Because the La^{3+} atoms posses no magnetic moment, the measured one has to be attributed to the (Fe_4Sb_{12})-polyanion. μ_{eff} = 2.4 μ_B/fu was obtained for $CeFe_4Sb_{12}$ [3]. The explanations for the magnetic behaviour are, as discussed by [1], still controversial. The Pr compound orders magnetically around 5 K with presumably some kind of antiferromagnetic spin alignment on the Pr ions and an effective moment of 2.7 μ_B on the (Fe_4Sb_{12}) building blocks, if a moment according to Pr^{3+} is assumed. As ground state for the Pr atoms the triplet Γ_5 was deduced [3 - 5]. The Nd and Eu compounds order magnetically at 13 K and appr. 84 K, with μ_{eff} = 4.5 and 8.4 μ_B, respectively [3]. An intermediate valence state is present in the Yb sample, for which μ_{eff} = 4.49 μ_B/fu was deduced [6].

From band structure calculations carried out on $LaFe_4Sb_{12}$ a double peak structure of the 3d-DOS in the proximity of the Fermi energy was obtained, from which the presence of a moment on the Fe atoms was concluded [7].

Results of Mössbauer investigations revealed, however, zero moment on the (Fe_4Sb_{12})-polyanion for the Ce skutterudite [8], and from experiments in external fields at 4.2 K followed either zero (for the Yb [6]) or very small induced hyperfine fields (B_{ind}) (for the Pr compounds [5]).

Thus generally large μ_{eff} values obtained from Curie-Weiss analysis, theoretical hints for Fe-moments, and contradictory small B_{ind} at low temperatures motivated the present study.

Experimental

Samples were prepared by arc melting under argon atmosphere using minimal electrical current to take into consideration the high vapor pressure of RE and Sb. After remelting for several times the ingots were sealed under vacuum in silica capsules, heated with 50°C/h to 700°C and kept there for 150 h followed by quenching in water. Details were described in [9].

The RE filling factor was determinated from X-ray powder diffraction data, obtained with a Huber-Guinier camera and Cu $K\alpha_1$ radiation, by using the program package FULLPROF.

Mössbauer measurements were carried out in transmission geometry at 4.2 K. External fields (B_a) up to 13.5 T (accuracy ± 0.01 T, homogeneity over a cylinder with 2 mm height and 15 mm diameter 0.1%) were produced by superconducting coils and controlled with a Hall probe. The field direction was always parallel to the γ-ray direction. The ^{57}Co**Rh** source (relative to which all centre shift (*CS*) values are given) was situated in a field-compensated region (less than 0.1 T). Their temperature varies in the course of the measurements between 5 and 25 K. An additional counter was mounted above the Mössbauer drive to allow simultaneous calibration measurements.

The spectra were analysed by solving the full Hamiltonian taking into account both electrostatic and magnetic hyperfine interactions. Sample thickness was considered using the approximation given by [10].

Results and discussion

The partly filled skutterudites $RE_xFe_4Sb_{12}$ belong to the space group $Im\overline{3}$ [e.g. 1 and ref. therein]. In this structure type the RE atoms occupy the 2*a*, the Fe atoms the 8*c* and the Sb atoms the 24*g* positions. From X-ray investigations both the Fe and the Sb sublattice are found to be fully occupied, whereas a considerable amount of vacancies was found to be present in the RE – sublattice (x = 0.80, 0.73, 0.72, and 0.88 for La, Pr, Nd, and Eu, respectively). Only for Yb the RE sublattice appears to be fully occupied [6]. Thus Fe may be surrounded by either two, one ore zero RE atoms assuming a statistical distribution in the nearest neighbour shell. These different surroundings can influence the hyperfine parameters leading to the asymmetry in the recorded spectra at zero field (examples for the Pr and Eu compounds are shown in Figs. 1 and 2. The third subspectrum in the spectra of the Eu sample, indicated by the dotted line, has to be attributed to an Fe containing impurity phase, which orders magnetically around 25 K [9]). For these spectra the analyses were only possible with a superposition of at least two subspectra (line widths always in the order of 0.22 mm/s) with different *CS* and quadrupole splitting *QS* (= $eQV_{zz}/4$). The relative intensities of these subspectra are in fair agreement with the void concentration determined by the X-ray investigations. Thus the spectrum with the higher intensity (Figs. 1, 2) may be allocated to Fe with two surrounding RE atoms and the other to Fe with one or two vacancies in the neighbourhood. This favours thus for the Fe skutterudites a statistical distribution of voids and RE atoms on the 2*a* sites. Although found in all investigated compounds, this behaviour does not seem to be general for all partly filled skutterudites since a solid solution of a completely filled Fe compound in a practically empty Co compound was assumed to be realized in $Ce_xFe_{4-y}Co_ySb_{12}$ [8, 11]. The spectra recorded in external fields were analysed with the restriction that the parameters for relative intensities

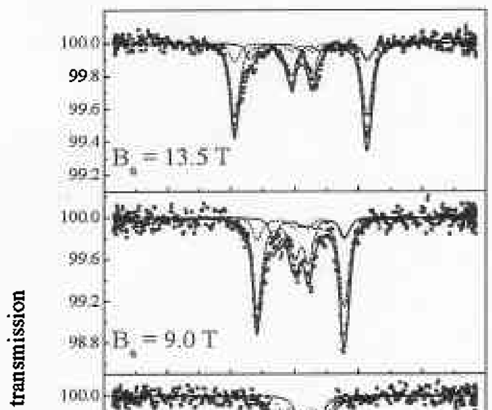

Figure 1: ^{57}Fe Mössbauer spectra of $Eu_{0.88}Fe_4Sb_{12}$ recorded at 4.2 K in various fields.

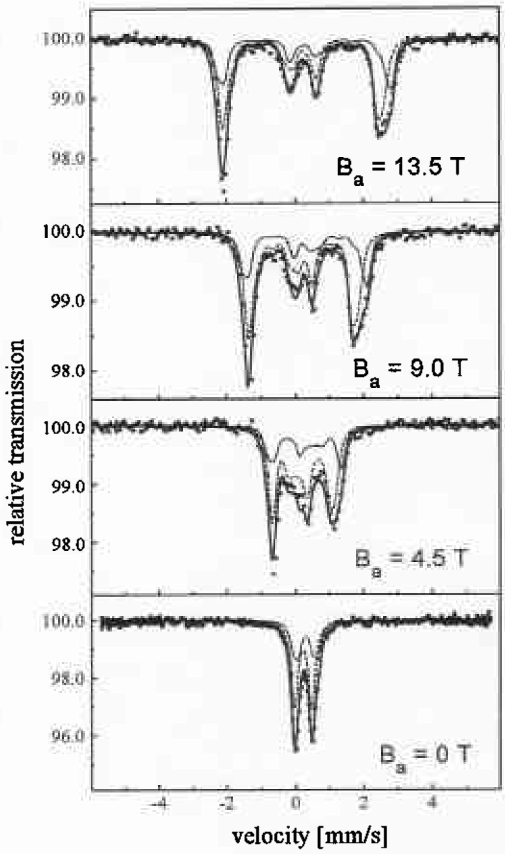

Figure 2: ^{57}Fe Mössbauer spectra of $Pr_{0.73}Fe_4Sb_{12}$ recorded at 4.2 K in various fields.

of the subspectra, *CS*, and *QS*, remain constant and only the measured hyperfine field (B_{hf}) changes due to the presence of the external field. Changes of the line width up to 10% were allowed (Figs. 1, 2). Above 4 T the measured spectra are fully polarised (the intensity of the $\Delta m = 0$ transitions vanishes).

The obtained *QS* values for the various RE compounds scatter around 0.25 mm/s (Fig. 3) and are different for the two Fe sites. For Fe surrounded completely by RE atoms the sign of the quadrupole splitting was in all analyses positive. Concerning the sign of *QS* obtained for Fe with voids in the RE shell no clear cut decision is possible from the present experiments. Analyses with both positive and negative sign lead to practically the same χ^2 values and for external fields around 4 T, where comparabel exchange energies of magnetic and electrostatic exchange interaction can be expected, always some small deviations between fit and measurement remained (Figs. 1, 2). In comparing all collected results, especially the ones for which spectra at different temperatures were recorded, a positive sign seems to be more reasonable.

Interesting to note that for both Fe sites the *QS* values for the Eu^{2+} skutterudite (e.g. at 4.2 K: 0.170 and 0.180 mm/s for Fe completely and partly surrounded by Eu atoms, respectively, Fig. 3) are approximately 35% smaller than those for the RE^{3+}

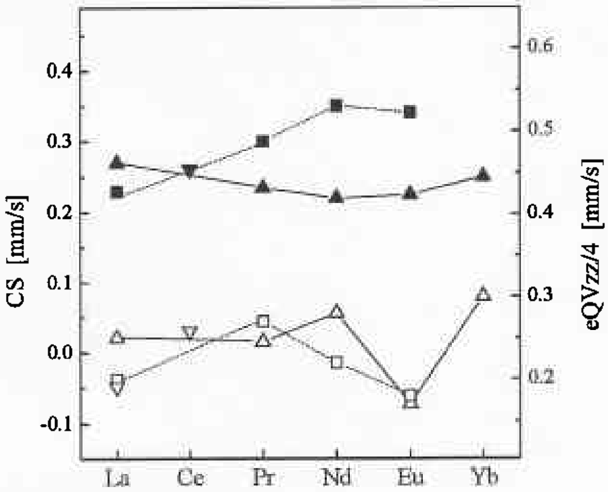

Figure 3: Centre shift *CS* (relative to ^{57}Co**Rh** at temperatures between 5 and 20 K, full symbols) and quadrupole splitting (open symbols) derived at 4.2 K for $RE_xFe_{14}Sb_{12}$. Fe completely (▲) and partly (■) surrounded by RE atoms. The lines are guides for the eyes. *CS* (▼) and *QS* (▽) after [8], values adapted for the present experimental conditions.

compounds (e.g. $Pr_{0.73}Fe_4Sb_{12}$ at 4.2 K: 0.245 and 0.270 mm/s for Fe completely and partly surrounded by Pr atoms, respectively, Fig. 3). This reflects the changes in the lattice constants (e.g. 9.1357 Å for the Pr and 9.1631 Å for the Eu compound [9]) and is in accordance with investigations of the temperature dependence of *QS* in $Eu_{0.88}Fe_4Sb_{12}$ [12].

Starting with $La_{0.80}Fe_4Sb_{12}$ the derived *CS* values for Fe completely surrounded by RE atoms decrease for the Pr and Nd compound (Fig. 3). The Eu^{2+} state does not lead to a significant change in *CS*. For the Yb sample an increase to 0.250 mm/s is obtained. This compound is found to be completely filled, thus only one spectrum remains in the analysis. The revers behaviour is found for Fe with voids in the RE shell. For this sites *CS* increases from La to Eu (Fig. 3). In performing the proper correction for the source temperature the values are in good agreement with the ones reported for the Ce compound [8], and indicate a rather similar *s* electron density at the Fe nucleus excluding the presence of a Fe^{2+} state.

The values of the measured hyperfine fields for the subspectrum allocated to Fe with two RE atoms in the neighbour shell either coincide with the one of B_a or were slightly larger (Fig. 4). Significant deviations from the value of B_a were only obtained for Fe atoms with voids in the RE neighbour shell. It should be mentioned that according to bulk magnetic measurements the Pr and the Nd compounds are magnetically ordered at the measuring temperature (ordering temperatures 5 K [4] and 13 K [3], respectively) whereas no magnetic order is observed in the La and Yb samples [3, 6]. An exception from this behaviour is present for the Eu compound, which is ferromagnetically ordered, up to appr. 84 K [3, 9]. For this compound the hyperfine fields for both Fe environments are negative, as one would expect for a ferromagnetically ordered compound (Fig. 4).

From $B_{ind} = B_{hf} - B_a$ the induced hyperfine fields were calculated. For Fe atoms with voids in the RE shell B_{ind} exibit some tendency towards a saturation at high applied fields, whereas for Fe completely surrounded by RE atoms B_{ind} scatters around zero (Fig. 5). Both contributions are, however,

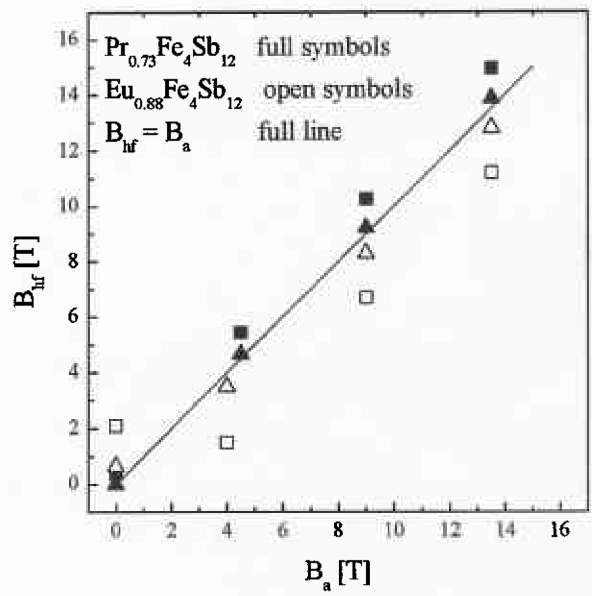

Figure 4: Dependence of the measured hyperfine fields B_{hf} on the external field B_a at 4.2 K. Fe completely (▲) and partly (■) surrounded by RE atoms.

too small to explain directly the large effective moment assigned to the (Fe_4Sb_{12}) building blocks from the bulk magnetic measurements at higher temperatures. These results contradict the simple picture based on charge counting arguments that these moments are due to the unpaired spin of Fe^{3+} in low spin configuration [3]. They strongly point to the necessity of a subdivision into a core and a valence contribution by proper band structure calculations. The opposite sign of these contributions allows a compensation which may explain the small values of B_{ind}. Only the core-field reflects the spin density at the ^{57}Fe nucleus and is thus directly proportional to the Fe moment. This compensation must, however, be present in all samples, irrespective of their magnetic ground state. High field Mössbauer investigations at elevated temperatures are currently in progress to gain additional information.

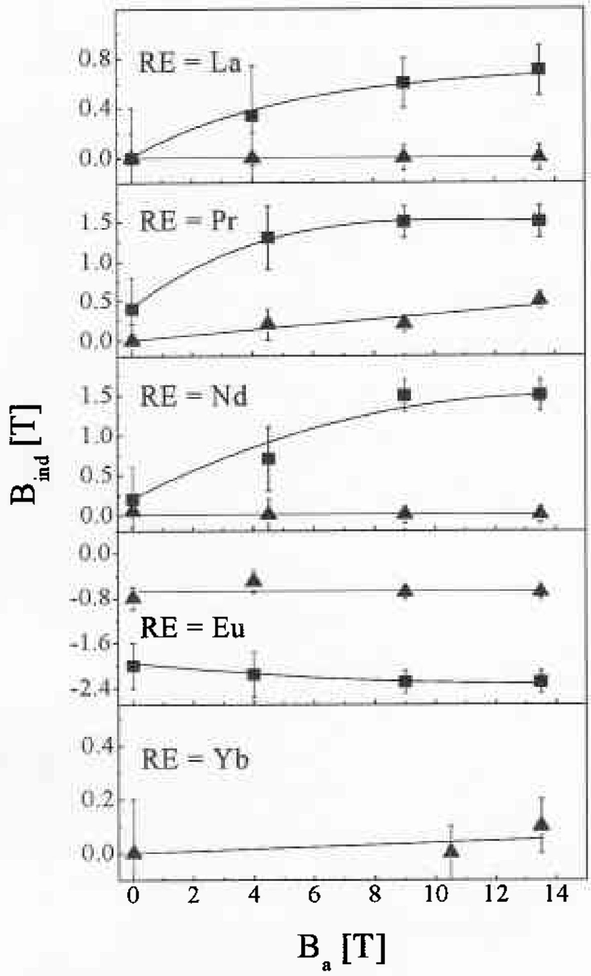

Figure 5: Field dependence of the induced hyperfine fields B_{ind} at 4.2 K for the investigated skutterudites $REFe_4Sb_{12}$. Fe completely (▲) and partly (■) surrounded by RE atoms. The lines are guides for the eyes.

Conclusions

Two Fe sites were identified, favoring a statistical distribution of voids and RE atoms on the 2*a* lattice positions. The relative intensities of these subspectra are in good accordance with the filling factor determined by X-ray investigations.

The quadrupole splitting reflects the changes of the lattice constant with varying RE atom.

The isomer shift data indicate a rather similar *s* electron density at the Fe nucleus and exclude the presence of a Fe^{2+} state.

The values of the induced hyperfine fields are much too small to explain directly the large effective moments deduced on the Fe sites from susceptibility measurements at high temperatures. Band structure calculations, currently under progress, are necesssary to decide if a compensation of core and valence contribution of the induced hyperfine field on the ^{57}Fe nucleus is able to account for this discrepancy.

Acknowledgments

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