Sb NQR in filled skutterudites MFe$_4$Sb$_{12}$ (M = Na, Ca, La)

A.A. Gippiusa,b,*, E.N. Morozova,a,b, K.S. Okhotnikov,a, E.A. Alkaev,a, A.V. Shevelkov,a, M. Baenitzb, A. Leithe-Jasperb, H. Rosnerb, R. Viennoisc,d, Yu. Grinb, F. Steglichb

aMoscow State University, 119992 Moscow, Russia
bMax-Planck-Institute for Chemical Physics of Solids, 01187 Dresden, Germany
cUniversité Montpellier II, 34095 Montpellier, France

Abstract

Temperature-dependent nuclear quadrupole resonance (NQR) investigations on the $^{121,123}$Sb nuclei in filled skutterudites MFe$_4$Sb$_{12}$ (M = Na, Ca, La) are reported. These new compounds show a nice interplay of ferromagnetic and antiferromagnetic correlations best seen in the relaxation rate. Substructures observed in the $^{121,123}$Sb NQR spectra give strong evidence for static (or dynamic) disorder on the filler site. Therefore, we performed ab-initio linearized augmented plane wave (LAPW) calculations for the Sb NQR substructure frequencies for various La and Ca displacement along different direction and compared the obtained values with the experimental data.

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1. Introduction

The filled skutterudites are the family of compounds possessing a peculiar crystal structure built of a framework formed by atoms from the Groups VIII and XV, which encapsulate a large lanthanide atom [1]. The renaissance of the interest into the filled skutterudites is clearly associated with the discovery of the prospective thermoelectric properties of these compounds. The early expectations based on the “phonon glass, electron crystal” (PGEC) concept proposed by Slack [2] had soon received the experimental support confirming that the filled skutterudite, especially those containing Sb as a Group XV element, possess high figures of merit indicating the efficiency of a thermoelectric material [3]. However, the microscopic origin of the thermoelectric properties remains unclear. In this work, we probe the local structure of the filled skutterudite, La$_{0.9}$Fe$_4$Sb$_{12}$, with the $^{121,123}$Sb NQR measurements.

2. Experiment

NQR spectra were obtained with standard coherent pulsed spectrometer using a point-by-point technique. The polycrystalline single-phase NaFe$_4$Sb$_{12}$ and CaFe$_4$Sb$_{12}$ samples, were prepared and characterized as described in Ref. [4]. The details of the synthesis, chemical and structural characterization for La$_{0.9}$Fe$_4$Sb$_{12}$ are reported in Ref. [5]. The existence of about 10% vacancies on the filler site (the (0,0,0) position of the Im3 space group) was found from the crystal structure refinement [6].

3. Results and discussion

There is a remarkable difference in Sb NQR spectra of these skutterudites. Whereas in NaFe$_4$Sb$_{12}$ all Sb NQR lines are narrow, in La$_{0.9}$Fe$_4$Sb$_{12}$ lines are much broader and exhibit additional singularities (substructure), which are most clearly seen at the 3/2–5/2 NQR transition ($v_2$ line) of $^{121}$Sb (Figs. 1 and 2). It seems natural to associate the strongest peak with the Sb nuclei in the Sb$_{12}$ cages with the La in the non-distorted (0,0,0) position and to assume that the substructure stems from the Sb nuclei in the cage.
with La vacancy in it and/or from the cages, which are nearest to the empty one. This substructure can not be explained by the coherent shift of the La atoms from the cubic position in [1,1,1] or [1,0,0] directions in an ideal stoichiometric LaFe$_4$Sb$_{12}$ since the calculated energy difference as a function of the La atom displacement (Fig. 3) is parabolic-like and does not exhibit any additional minimum.

We note that the Sb NQR spectrum in CaFe$_4$Sb$_{12}$ is intermediate between those of NaFe$_4$Sb$_{12}$ and La$_{0.9}$Fe$_4$Sb$_{12}$ and the quadrupole substructure is already observable. That means that the effect of the filler atom distortion and/or disposition appears already in skutterudites with alkali-earth filler atom.

In conclusion, $^{121,123}$Sb NQR results combined with ab-initio LAPW calculations provide a new experimental indication for the presence of local distortions of La position in the crystal structure of the non-stoichiometric La$_{0.9}$Fe$_4$Sb$_{12}$. This effect is probably caused by the local La displacement induced by nearest La vacancies.

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References