Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 378–380 (2006) 239–240
PHYSICA B
www.elsevier.com/locate/physb

Sb NQR in filled skutterudites MFe_4Sb_{12} (M = Na, Ca, La)

A.A. Gippius[a,b,*], E.N. Morozova[a,b], K.S. Okhotnikov[a], E.A. Alkaev[a], A.V. Shevelkov[a], M. Baenitz[b], A. Leithe-Jasper[b], H. Rosner[b], R. Viennois[b,c], Yu. Grin[b], F. Steglich[b]

[a]*Moscow State University, 119992 Moscow, Russia*
[b]*Max-Planck-Institute for Chemical Physics of Solids, 01187 Dresden, Germany*
[c]*Université Montpellier II, 34095 Montpellier, France*

Abstract

Temperature-dependent nuclear quadrupole resonance (NQR) investigations on the ^{121,123}Sb nuclei in filled skutterudites MFe_4Sb_{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.
© 2006 Elsevier B.V. All rights reserved.

PACS: 76.60.Gv; 71.15.Ap

Keywords: NQR; Skutterudites

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, $La_{0.9}Fe_4Sb_{12}$, with the ^{121,123}Sb NQR measurements.

*Corresponding author. Moscow State University, 119992 Moscow, Russia. Fax: +7 095 3625576.
E-mail address: gippius@mail.ru (A.A. Gippius).

0921-4526/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2006.01.090

2. Experiment

NQR spectra were obtained with standard coherent pulsed spectrometer using a point-by-point technique. The polycrystalline single-phase $NaFe_4Sb_{12}$ and $CaFe_4Sb_{12}$ samples, were prepared and characterized as described in Ref. [4]. The details of the synthesis, chemical and structural characterization for $La_{0.9}Fe_4Sb_{12}$ 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 $NaFe_4Sb_{12}$ all Sb NQR lines are narrow, in $La_{0.9}Fe_4Sb_{12}$ lines are much broader and exhibit additional singularities (substructure), which are most clearly seen at the 3/2–5/2 NQR transition (ν_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

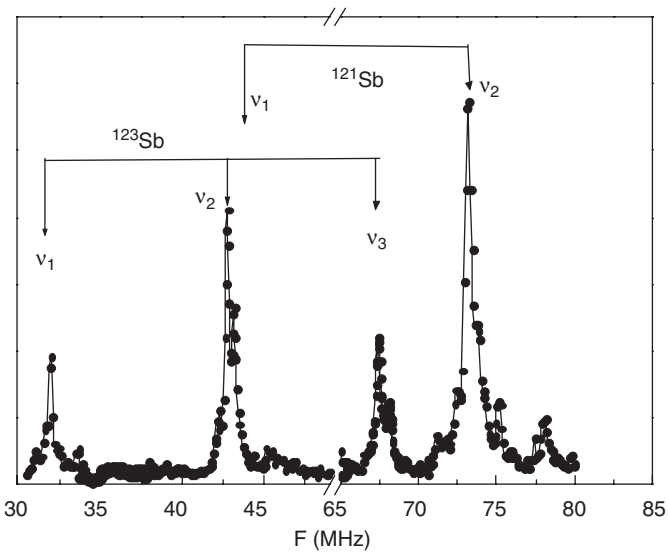

Fig. 1. ^{121,123}Sb NQR spectrum of $La_{0.9}Fe_4Sb_{12}$ at 15 K.

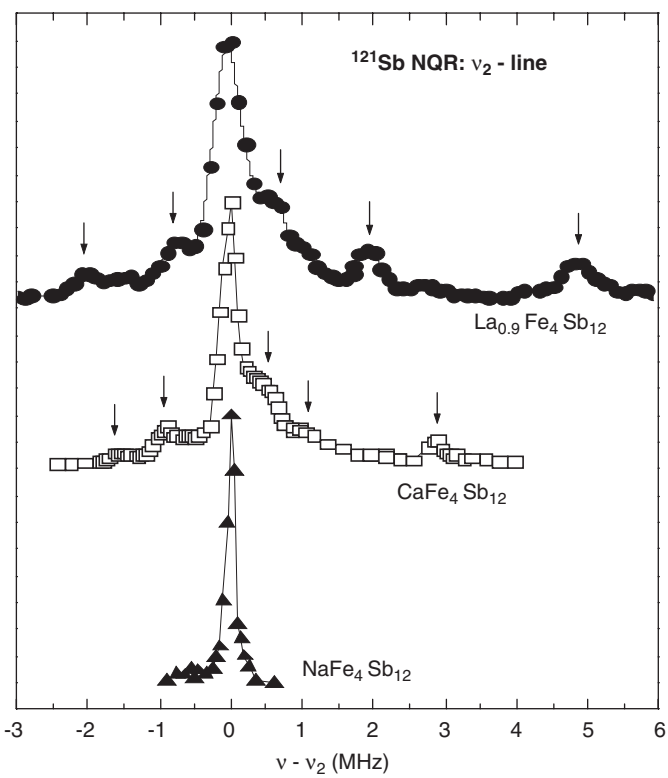

Fig. 2. ^{121}Sb ν_2 lines in $La_{0.9}Fe_4Sb_{12}$, $CaFe_4Sb_{12}$ and $NaFe_4Sb_{12}$ For each spectrum the frequency axis is shifted with respect to the ν_2 values. Arrows indicate the positions of substructure lines.

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

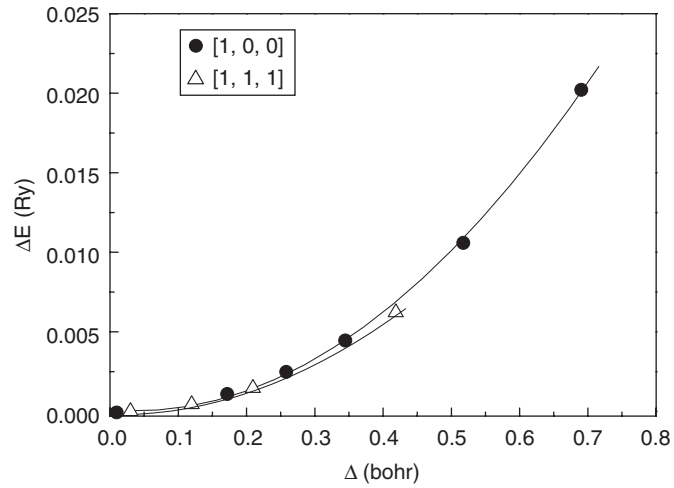

Fig. 3. LAPW calculated energy difference for stoichiometric $LaFe_4Sb_{12}$ structure with La atom shifted along [1,0,0] and [1,1,1] directions and the non-shifted case (La in the position (0,0,0)). Solid lines are the best fit to the function $\Delta E \sim \Delta^2$.

stoichiometric $LaFe_4Sb_{12}$ 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 $CaFe_4Sb_{12}$ is intermediate between those of $NaFe_4Sb_{12}$ and $La_{0.9}Fe_4Sb_{12}$ 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 $La_{0.9}Fe_4Sb_{12}$. This effect is probably caused by the local La displacement induced by nearest La vacancies.

E.N.M. thanks Grant MK-1212.2005.2.

References

[1] D.J. Braun, W. Jeitschko, J. Less, Common Met 72 (1980) 147.
[2] G.A. Slack, CRC Handbook of Thermoelectrics, in: D.M. Rowe (Ed.), Chemical Rubber, Boca Raton, FL, 1995.
[3] B.C. Sales, D. Mandrus, R.K. Williams, Science 272 (1996) 1325.
[4] A. Leithe-Jasper, W. Schnelle, H. Rosner, M. Baenitz, A. Rabis, A.A. Gippius, E.N. Morozova, H. Borrmann, U. Burkhardt, R. Ramlau, U. Schwarz, J.A. Mydosh, Y. Grin, V. Ksenofontov, S. Reiman, Phys. Rev. B 70 (2004) 214418.
[5] L. Chapon, D. Ravot, J.C. Tedenac, J. Alloys Compounds 282 (1999) 58.
[6] R. Viennois, D. Ravot, F. Terki, C. Hernandez, S. Charar, P. Haen, S. Paschen, F. Steglich, J. Magn. Magn. Matter 272–276 (2004) e113.