	Experiment title: ^{121}Sb nuclear inelastic scattering study of thermoelectric $Yb_{14}MnSb_{11}$, $YbFe_4Sb_{12}$, and Sb_2Te_3	Experiment number: HE 3051
Beamline: ID22N	**Date of experiment**: from: May 12th 2009 to: May 19th 2009	**Date of report**: Sept 4th 2009
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Names and affiliations of applicants (* indicates experimentalists):

R. P. Hermann,[1,2,*] A. Möchel[1,2,*], T. Claudio[1,2,*], I. Sergeev[3,*], H.-C. Wille[4,*]

1. Institut für Festkörperforschung, JCNS und JARA-FIT, Forschungszentrum Jülich, Jülich, Germany
2. Departement de Physique et Departement de Chimie, Université de Liège, Liège, Belgique
3. European Synchrotron Radiation Facility, Grenoble, France
4. Hasylab, DESY, Hamburg, Germany

Report:

We have carried out measurements of the antimony specific nuclear inelastic scattering in several antimony bearing thermoelectric compounds using a backscattering sapphire monochromator cooled to match the resonance energy. Progress was achieved in the methodology and spectra with good statistics were collected for all proposed samples.

Improvements of the technique: significant time during the proposal, ~10 shifts, was devoted to systematically inspect different spots of the sapphire, because the initial resolution turned out to be too poor, ~6-7 meV. Finally a good spot was found, which allowed us for the first time to reach a ~1.2 meV resolution, with a very reproducible resolution function, the quality of which was not modified during the last 8 shifts. Further, on the nuclear resonance, we observed a largely increased count rate in the nuclear forward scattering channel, reaching >50 Hz. These improvements were possibly essentially by adding a bender as optical element in the beam path, in order to achieve a reasonable degree of horizontal focusing. Good results were obtained only with a beamspot of ca. 400 x 400 µm^2 on the sapphire crystal.

Results of the nuclear inelastic scattering results on the sample: we grouped in this proposal the measurements on three antimony bearing thermoelectric materials A) $Yb_{14}MnSb_{11}$, B) $YbFe_4Sb_{12}$, C) Sb2Te3 and PbTe/Sb_2Te_3 nanolamellae. The context of these measurements and the results can be summarized as follows:

A) $Yb_{14}MnSb_{11}$ has been recently shown to be the most promising thermoelectric material for high temperature conversion of thermal to electrical energy[1]. The thermal conductivity is exceptionally low, which is one property that a material must exhibit in order to be an effective thermolectric material. In order to complete the information obtained by neutron scattering, dominated by the Yb scattering, and to verify the absence of high energy phonons that was indicated by the neutron scattering at high temperature, we measured the ^{121}Sb partial DOS at 25 K, see Fig. 1. We indeed observe that, in agreement with the low Debye temperature of ~160 K, but in sharp contrast with the still undetermined high melting temperature, above 1200 °C, no high energy Sb phonons are observed.

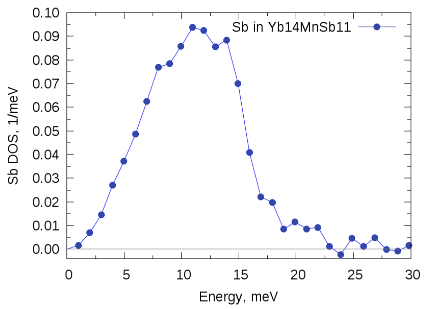

Fig. 1. Sb partial DOS in $Yb_{14}MnSb_{11}$.

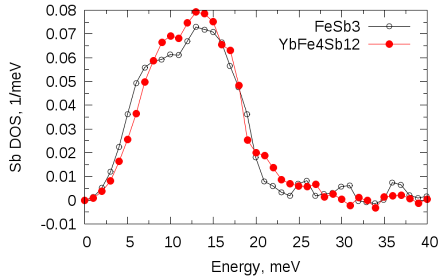

Fig. 2. Comparison of the Sb partial DOS in $YbFe4Sb_{12}$ and $FeSb_3$

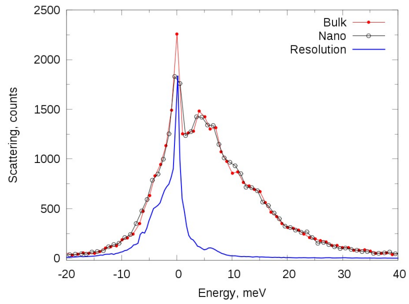

Fig. 3. NIS in bulk and “nano” Sb_2Te_3

B) In $YbFe_4Sb_{12}$ elastic constant measurements and inelastic neutron scattering measurements indicate an anomalous softening at ~50 K[2]. Filled skutterudites, and in particular iron-antimony and iron-osmium skutterudites have attracted an exponentially growing interest in the last 10 years, with over 140 published papers in 2007. Several studies of the lattice dynamics in filled skutterudites show that the signature of the 'rattler' mode is essentially that of an Einstein oscillator[3], and we have recently completed this model with ^{121}Sb NIS in $EuFe_4Sb_{12}$, measurements that revealed the coupling between host and guest vibrations[4]. However, $YbFe_4Sb_{12}$ appears to present a richer behavior, as it exhibit a peculiar softening around 50 K. Our current hypothesis to explain this softening is a reorganization of the phonon spectrum, the origin of which is so far unknown. We have measured the antimony 121 NIS at 25 K, and, as a potential reference sample, we also measured the nuclear inelastic scattering by the empty skutteride $FeSb_3$, see Fig. 2.

C) $PbTe/Sb_2Te_3$ nanolamellae[5] are promising systems in which nanostructuration can lead to low thermal conductivity, that improves their thermoelectric figure of merit. The work on such nanostructured materials follows from the proposal by Dresselhaus *et al.* that phonon and electron confinement can be used to doubly benefit the thermoelectric figure of merit by both increasing the Seebeck coefficient and decreasing the thermal conductivity. Herein, we proposed to conduct the first study of the influence of this nanostructuration on the phonon spectra. In order to get a microscopic insight into the observed modification of the macroscopic properties. We have measured the ^{121}Sb partial phonon DOS in bulk Sb_2Te_3 polycristalline material, in nanostructured Sb_2Te_3 obtained by spark plasma sintering, and in $PbTe/Sb_2Te_3$ nanolamellae, see Fig. 3. No significant differerences in the DOS is observed, most likely because the nanostructures were too large (200 nm) for any confinement effect to be observed at the accessible energy range.

In summary, owing to the breakthrough in methodology achieved during this proposal, the use of sapphire backscattering monochromators for high resolution nuclear inelastic scattering appears now to reach maturity, as we could both achieve significant improvements in the resolution and reproducibility in the shape of the resolution function; further, the thermal control of the monochromator also proved very reliable. The main hurdle to be taken is now to obtain better single crystal sapphire, possibly specifically cut for a particular reflection. The detailed analysis of the density of states of the measured samples is ongoing, and so far the only firm conclusion that can be drawn is that the (metastable) empty skutterudite $FeSb_3$ proved significantly softer than the (stable) $CoSb_3$ compound, and as such, $FeSb_3$ is not a good reference for the lattice dynamics in the filled skutterudites.

[1] S. R. Brown et al., Chem. Mater. 18, 1873 (2006).
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[4] Wille H.-C. *et al.*, *Phys. Rev. B* **76**, 140301(R) (2007). (Highlighted in the ESRF Annual Report 2008)
[5] T. Ikeda et al., Chemistry of Materials 19(4) pp 763 - 767 (2007).