| ESRF | **Experiment title:** An Sb-121 Nuclear Inelastic Scattering Study of Zn4Sb3 | **Experiment number:** HS-3041 |
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| **Beamline:** ID22N | **Date of Experiment:** from: 04/07/2006 to: 26/07/2006 | **Date of Report:** August 14, 2007 |
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## Report:

The observation of nuclear resonant scattering from $^{121}$Sb at the 37.13 keV [1] in the experiment MI-710 provided a route for the realization of the first nuclear inelastic scattering (NIS) measurements on antimony in the recent experiment HS-2928. During the experiment HS-3041, on which we report here, dynamical studies on $Zn_4Sb_3$ using this technique have been performed, and data quality on $CoSb_3$ has $EuFe_4Sb_{12}$ has been improved. To our knowledge these have been the first dynamical studies using this technique for a nuclear transition energy above 30 keV in general, and for $^{121}$Sb in particular. The high resolution monochromatization in the meV range at 37.13 keV required in order to resolve the phonon spectra was achieved by a sapphire Bragg backscattering monochromator [1,2]. The energy of the reflected radiation is modulated by changing the temperature of the sapphire crystal both above and below 146.54 K, the temperature corresponding to the $E_0$=37.1298(2) keV Mössbauer resonance energy in $^{121}$Sb. At this temperature, the variation in the backscattered photon energy is 59.6 meV/K. Technical improvements have reduced the energy resolution of the monochromator from 7.0 meV achieved in the experiment HS2928 to 4.5 meV (see NFS spectra in Fig. 1a and 2a). The polycrystalline powdered samples were placed in a closed cycle cryostat at an estimated temperature of 25 K. The vibrational density of states (DOS) of the samples have been extracted from the measured NIS spectra (Fig. 1a and 2a) and are shown in Fig. 1b and 2b.

The comparison of the DOS in filled ($EuFe_4Sb_{12}$) and unfilled ($CoSb_3$) skutterudites is of high interest for the understanding of the lattice dynamics in skutterudites, materials that are widely studied owing to their interesting thermoelectric properties. Fig. 1 shows the DOS of $CoSb_3$ and the DOS of $EuFe_4Sb_{12}$ compared to earlier calculations performed for $LaFe_4Sb_{12}$, calculations that are now supported by our experimental data.

In conjunction with earlier $^{57}$Fe and $^{151}$Eu measurements, the $^{121}$Sb results provide a complete picture of the element specific DOS in $EuFe_4Sb_{12}$. The difference of the DOS of $CoSb_3$ and the DOS of $EuFe_4Sb_{12}$, shown in Fig. 1c, reveals a hybridization in the Sb DOS with an Eu mode at 7 meV (Fig. 1d) and a surprizingly small coupling of the host lattice with the Eu guest. This coupling is however sufficient to reduce the lattice thermal conductivity effectively [2].

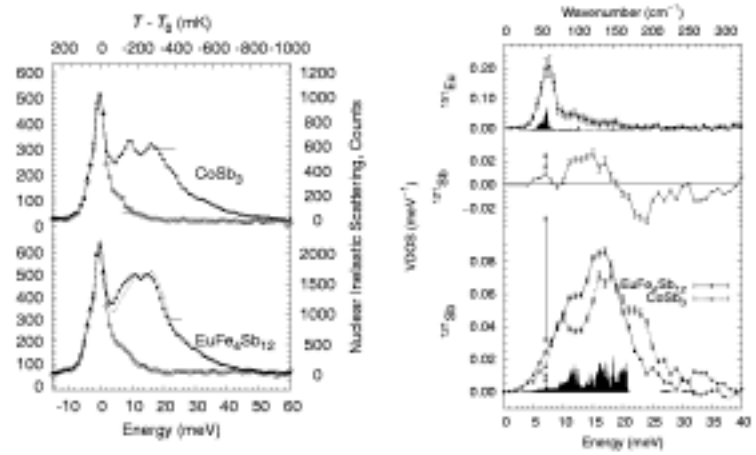


Fig. 1: To the left: the $^{121}$Sb NFS and NIS spectra of $CoSb_3$ and $EuFe_4Sb_{12}$. To the right: lower part: the Sb DOS in $CoSb_3$ and $EuFe_4Sb_{12}$ and the calculated Sb DOS in $LaFe_4Sb_{12}$ (scaled for visiblity). Middle part: the difference of the DOS $EuFe_4Sb_{12}$ minus $CoSb_3$. Upper part: the Eu DOS in $EuFe_4Sb_{12}$ and the calculated La DOS in $LaFe_4Sb_{12}$ (scaled for visiblity).

The NIS spectrum in $Zn_4Sb_3$ reveals that Sb participates significantly in a low lying localized vibrational mode at ca. 6 meV. Comparison with earlier inelastic neutron scattering data and theoretical calculations is ongoing. The presence of such a localized mode is similar to the localized Eu vibrational mode in $EuFe_4Sb_{12}$. This observation in $Zn_4Sb_3$ suggests that this type of mode is not restricted to materials that exhibit cage structures and might be a universal feature in materials that exhibit low lattice thermal conductivity, such as $Zn_4Sb_3$ and other thermoelectric materials.

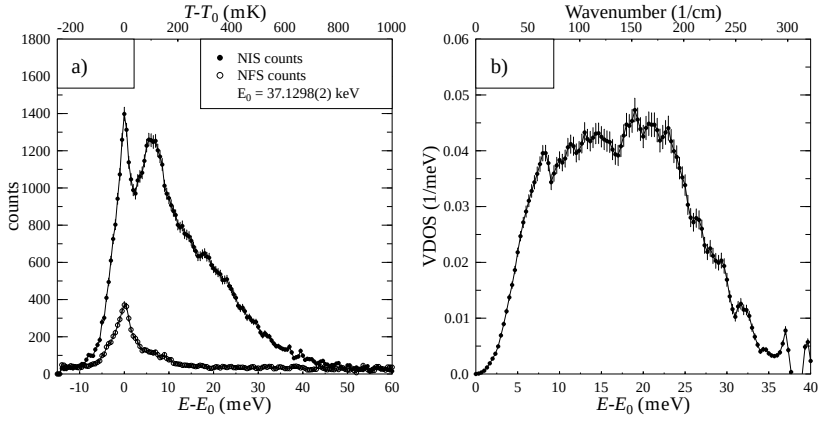


Fig. 2: a) The $^{121}$Sb NFS and NIS spectra of $Zn_4Sb_3$. b) The Sb DOS in $Zn_4Sb_3$.

## References

[1] H.-C. Wille, Yu. V. Shvyd'ko, E. E. Alp, H. D. Rüter, O. Leupold, I. Sergueev, R. Rüffer, A. Barla, J. P. Sanchez , Europhys. Lett., 74, no.1 (170)

[2] H.-C. Wille, R.P. Herrmann, I. Sergueev, O. Leupold, P. van der Linden, B.C. Sales, F. Grandjean, Gary J. Long, R. Rüffer, Yu. V. Shvyd'ko, submitted to Physical Review Letters.