A Europium-151 Nuclear Resonance and Neutron Scattering Study of Localized Vibrational Modes in Thermoelectric Materials

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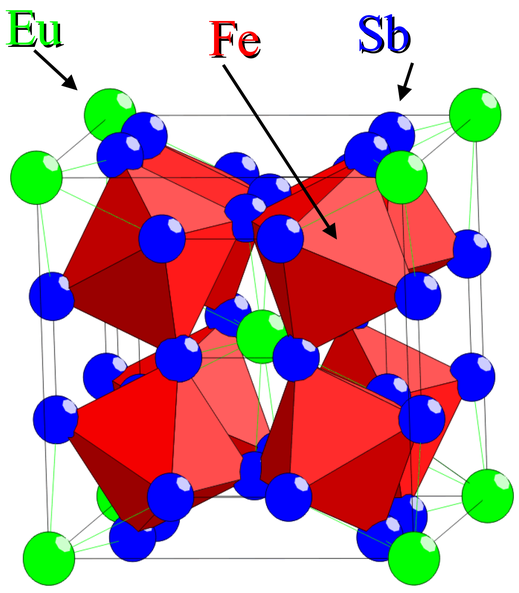
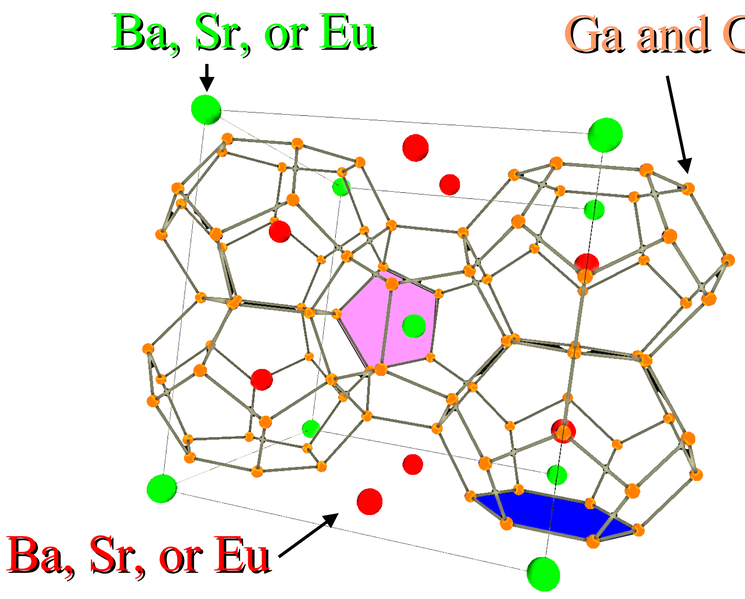


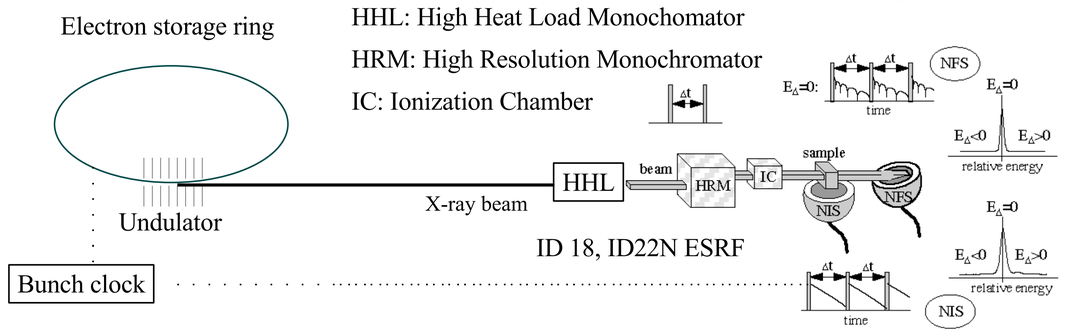
Filled antimony skutterudite

- Efficient thermoelectric materials must behave as a "phonon-glass" and an "electron-crystal".
- The insertion of loosely bound guests into cagey structures, such a skutterudites or clathrates, yields a reduction of the lattice thermal conductivity without reduction of the electric conductivity.
- **What are the characteristics of the vibrational modes of these loosely bound guests?**

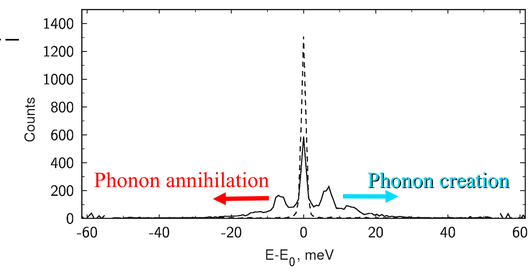


Filled $A_8Ga_{16}Ge_{30}$ type I clathrate

Experimental Techniques



Nuclear forward scattering - - - yields the resolution of the monochromator system and indicates the zero energy transfer point, E_0.



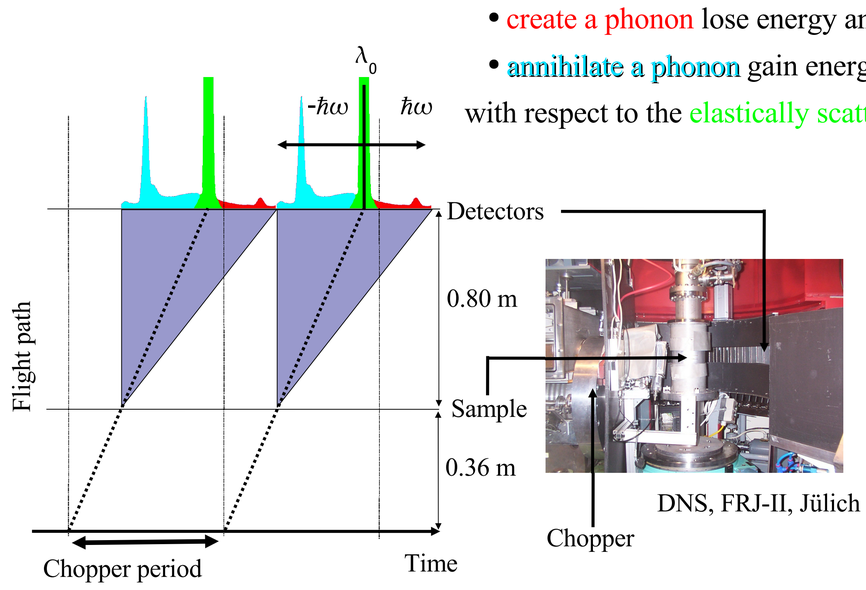
— Nuclear inelastic scattering reveals the phonon creation and annihilation processes in which the resonant nucleus takes part.

Nuclear Inelastic Scattering

The inelastically scattered neutrons that

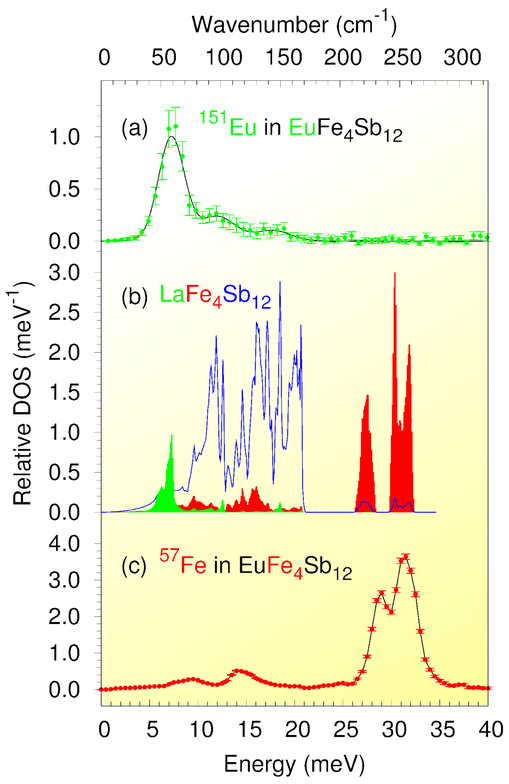
- create a phonon lose energy and arrive late,
- annihilate a phonon gain energy and arrive early,

with respect to the elastically scattered neutrons.

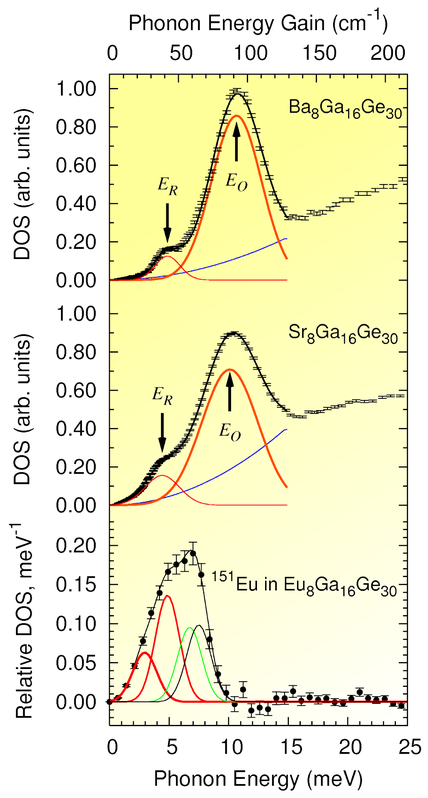


Inelastic Neutron Scattering

Results

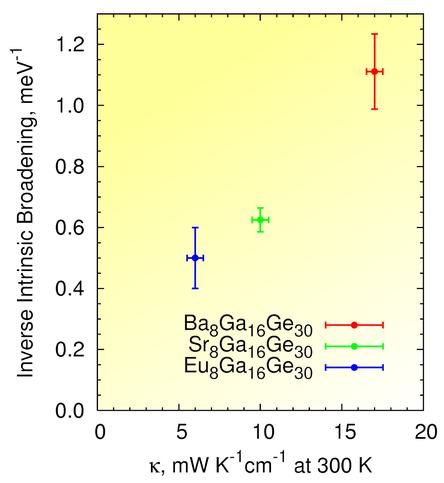


- The obtained densities of phonon states reveal that the caged guests exhibit essentially **localized vibrational modes at 5-7 meV**.
- In $EuFe_4Sb_{12}$, secondary peaks that result from the hybridization with Sb vibrational modes are observed. ^{121}Sb nuclear inelastic scattering measurements are ongoing.
- The localized vibrational modes of Ba and Sr, with energy E_R, in the larger clathrate cages are separated from the large optical phonon peaks at E_O, peaks which hide the vibrational modes of the guests in the smaller clahrate cages.
- Because the Eu in the larger clathrate cages of $Eu_8Ga_{16}Ge_{30}$ is located off-center, three different vibrational modes are observed, in addition to a single mode associated to the guests in the smaller dodecahedral cages.



Discussion

- The observed energies of the localized vibrational modes are in good agreement with previous EXAFS, Raman, and heat capacity measurements and *ab initio* calculations, for example in $LaFe_4Sb_{12}$.
- In all studied materials, **the localized vibrational modes are broader than the instrumental resolution**. The average time between collisions with the acoustic phonons can be obtained from the intrinsic broadening.
- Because the lattice thermal conductivity, κ, is proportional to the average time between phonon collisions, **κ is inversely proportional to the intrinsic broadening**. The *anharmonic* interactions that lead to the broadening of the localized vibrational modes are the likely cause of the reduction in thermal conductivity.



References

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And references therein.