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Strongly decoupled europium and iron vibrational modes in filled skutterudites

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The europium partial vibrational density of states (DOS) in $EuFe_4Sb_{12}$ and the iron partial vibrational DOS in both $EuFe_4Sb_{12}$ and $Ce^{57}Fe_4Sb_{12}$ have been obtained by nuclear inelastic scattering. The results reveal the strong independence of the iron and rare-earth vibrational modes. The cage filling europium only participates significantly to the low-energy local vibrational modes. The force constants have been obtained from the measured probability of nuclear absorption. The energies of the peaks in the europium and iron DOS are in excellent agreement with the calculated DOS in $LaFe_4Sb_{12}$. The results indicate that nuclear inelastic scattering is the technique of choice for the study of the localized vibrational modes in thermoelectric "phonon glass" materials.

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I. INTRODUCTION

A highly efficient thermoelectric material must behave as both a phonon glass and an electron crystal.[1] Filled antimony skutterudites, with the RM_4Sb_{12} generic formula, are promising materials for thermoelectric power generation because they exhibit both a good electrical conductivity and a reduced thermal conductivity. This combination of properties is believed to result from the presence of a localized vibrational mode attributed to the isolated rattling motion of the guest, R, filling the cubic lattice voids in RM_4Sb_{12}. Refs. 2–4 While the low thermal conductivity of the clathrates has been theoretically shown[5] to result from the presence of a localized vibrational mode at low energy, there is no theoretical or experimental proof of this correlation in the filled skutterudites. However, the decrease in thermal conductivity of the $Tl_xCo_{4-y}Fe_ySb_{12-z}Sn_z$ with thallium filling ratio brings an indirect and experimental support to this correlation.[6]

The design of optimized thermoelectric materials requires an in-depth understanding of the lattice dynamics and more specifically of the dynamics of each specific element in the lattice. However, to date, no direct experimental characterization could unambiguously assign the local vibrational mode observed in the density of states (DOS) of filled skutterudites to the filling atom, because the previous measurements were not element specific. The independence of the localized vibrational modes of the filling element or their hybridization with those of the cubic M_4Sb_{12} lattice is still a subject of controversy, because the lack of a strong interaction of the filling element with the framework seems incompatible with the strong reduction in the thermal conductivity observed[4,7,8] upon filling the structure. Among the available experimental techniques, only the recently developed[9] nuclear inelastic scattering technique can provide access to the *partial* density of vibrational states of a specific atom, albeit an atom which must have a Mössbauer active nuclide. The filled skutterudites are very amenable to such studies as they may simultaneously contain up to three Mössbauer active nuclides, iron-57 and antimony-121 in the basic skutterudite framework and europium-151 as the filling guest.

Herein, we demonstrate that nuclear inelastic scattering yields the high-resolution, element-specific, density of states for compounds as complex as the filled RM_4Sb_{12} skutterudites. Specifically, the vibrational behavior of the rare-earth, R=Eu, and of M=Fe, are separately observed. When combined with vibrational DOS calculations,[10] these nuclear inelastic scattering measurements yield an in-depth understanding of the element-specific dynamic properties of filled skutterudites.

In contrast to other methods used to study lattice dynamics, such as inelastic neutron scattering,[3] nuclear inelastic scattering, unlike conventional Mössbauer spectroscopy, measures the phonon-assisted nuclear absorption. As a consequence, nuclear inelastic scattering studies yield a partial phonon density of states that is ideally averaged and does not depend on the accessible part of reciprocal space.[9,11] However, as a drawback, the phonon dispersion cannot be measured by this technique. Further, nuclear inelastic scattering benefits from the Mössbauer-effect resonant nature of the interaction and permits a study of the vibrations of an isotope specific element within a complex polyatomic lattice, in our case vibrations involving iron-57 and europium-151. Finally, the study by inelastic neutron scattering of europium containing compounds is virtually impossible, and hence nuclear inelastic scattering is the technique of choice for such compounds.

II. EXPERIMENTAL

The nuclear inelastic scattering measurements on $Ce^{57}Fe_4Sb_{12}$ have been carried out at 295, 80, and 10 K (Ref. 11) with a resolution of 1 meV on beam line 3ID at the Advanced Photon Source at Argonne National Laboratory. The data analysis has been carried out with the PHOENIX program.[12] The iron-57 nuclear inelastic scattering measurements on $EuFe_4Sb_{12}$ have been carried out at 295 K with a resolution of 0.9 meV and the europium-151 measurements have been carried out at 25 and 295 K with a resolution of 1.6 meV on beam line ID18 and ID22N, respectively, at the European Synchrotron Radiation Facility in Grenoble, France.[13] The data analysis has been carried out with the INES program implemented in IDL code according to the theory of Kohn and Chumakov.[14]

High quality, low-temperature, nuclear inelastic scattering measurements are facilitated by an iron-57 enriched sample and we have elected to use $Ce^{57}Fe_4Sb_{12}$, a compound that is easily accessible[15] in a highly pure form on a small scale. In contrast, the synthesis of $Eu^{57}Fe_4Sb_{12}$ on a small scale is difficult, problematic, and cost prohibitive. The fully iron-57 enriched $Ce^{57}Fe_4Sb_{12}$ gave an iron-57 transmission Mössbauer spectrum identical to that previously observed.[16] The natural isotopic abundance $EuFe_4Sb_{12}$ sample was prepared as previously described[17] and characterized[18] by iron-57 and europium-151 transmission Mössbauer spectroscopy.

III. NUCLEAR INELASTIC SCATTERING RESULTS

The europium-151 partial DOS in $EuFe_4Sb_{12}$, obtained at 25 K by nuclear inelastic scattering, is shown in Fig. 1(a) and the iron-57 iron partial DOS in $EuFe_4Sb_{12}$ and $Ce^{57}Fe_4Sb_{12}$, obtained at 295 K by nuclear inelastic scattering, are shown in Figs. 1(d) and 1(e), respectively. The difference in the signal to noise ratio in the latter two figures illustrates the beneficial effect of iron-57 enrichment. The iron-57 partial DOS measured at 80 and 10 K in $Ce^{57}Fe_4Sb_{12}$ are virtually identical, as would be expected in the absence of any phase transition with temperature. The iron partial density of states consists of two main peaks at ca. 29 and 33 meV and much smaller contributions at 9 and 15 meV. The relative intensities of these four peaks are independent of the nature of the rare-earth guest rattler. In contrast, the energies of these peaks are ca. 0.5-meV smaller in $EuFe_4Sb_{12}$ than in $Ce^{57}Fe_4Sb_{12}$, a shift in energy that results from the larger unit-cell volume of $EuFe_4Sb_{12}$. These results are in excellent agreement with the calculations of the DOS in $LaFe_4Sb_{12}$ reported by Feldman *et al.*[8,10,19] [see Fig. 1(c)]. These calculations yield two main peaks at ca. 27.5 and 31 meV, peaks that are assigned to iron in the framework lattice. Recent inelastic neutron scattering measurements[20] indicate that the calculated iron vibrational energies in $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ are too low by approximately 2–3 meV, in perfect agreement with our experimentally observed 29 and 33 meV. A combination of the measured and calculated iron vibrational DOS reveals, first, that the iron vibrations are mainly localized in the same two regions at high, ca. 30 meV, and low, ca. 14 meV, energies separated by a gap and are essentially independent of the filling atom, La, Ce, or Eu.

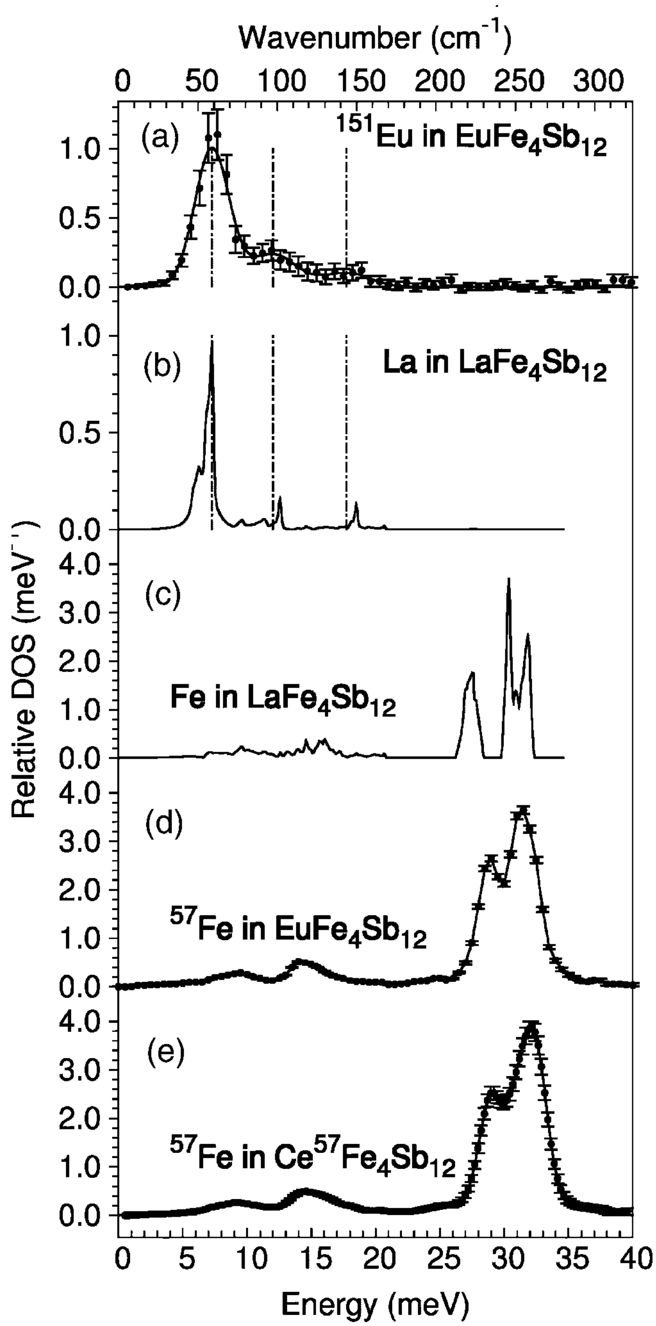

FIG. 1. (a) The europium partial DOS in $EuFe_4Sb_{12}$ obtained at 25 K by europium-151 nuclear inelastic scattering. The solid line is a fit with three Gaussian peaks with energies of 7.3±0.1, 12.0±0.4, and 17.8±0.5 meV and linewidths of 3.2±0.2, 4.4±0.7, and 4.4±0.7 meV. (b) The La projected vibrational DOS in $LaFe_4Sb_{12}$, calculated by Feldman *et al.* (Ref. 19). (c) The Fe projected vibrational DOS in $LaFe_4Sb_{12}$, calculated by Feldman *et al.* (Ref. 19). (d) The iron partial DOS in $EuFe_4Sb_{12}$ obtained at 295 K by iron-57 nuclear inelastic scattering. (e) The iron partial DOS in $Ce^{57}Fe_4Sb_{12}$ obtained at 295 K by iron-57 nuclear inelastic scattering.

The europium-151 partial DOS of $EuFe_4Sb_{12}$, obtained at 25 K and shown in Fig. 1(a), has been fit with three Gaussian peaks with energies of 7.3±0.1, 12.0±0.4, and

TABLE I. Force constant and Lamb-Mössbauer factor in RFe_4Sb_{12}.

R	Atom	T (K)	Force constant (N/m)	Lamb-Mössbauer factor
Eu	Eu	295	48(44)	0.257(63)
	Eu	25	82(20)	0.788(18)
Ce	Fe	295	202(10)	0.760(5)
	Fe	80	164(6)	0.875(4)
	Fe	10	156(4)	0.897(2)
La	La		45[a]	
	Fe		172[a]	

[a]Data obtained from Ref. 10.

17.8±0.5 meV, with relative areas of 3.4±0.2, 1.1±0.2, and 0.5±0.1, and with linewidths of 3.2±0.2, 4.4±0.7, and 4.4±0.7 meV, where the last two linewidths have been constrained to be the same. These energies are in excellent agreement with the energies of 7.1, 12.4, and 18.5 meV calculated[10,19] for the La projected vibrational density of states in $LaFe_4Sb_{12}$ [see Fig. 1(b)]. Further, the energies of the first two peaks agree well with those observed[2] by inelastic neutron scattering in $LaFe_4Sb_{12}$. The peak at 7.3 meV is characteristic of the Einstein behavior of europium in $EuFe_4Sb_{12}$. However, this peak occurs at an energy smaller than the calculated[8] "bare" Einstein energy of 9 meV for La in $LaFe_4Sb_{12}$. Its experimental width of 3.2 meV corresponds to a natural width of 2.7 meV when the experimental resolution of 1.6 meV and the quadratic addition of the widths are taken into account. This natural width is larger than that observed[3] for the localized vibrational mode of Tl in $Tl_{0.8}Fe_3CoSb_{12}$ and is similar to that observed[3] in $Tl_{0.8}Co_4Sb_{11}Sn$. Both the lower than calculated Einstein energy and the small width of the europium vibrational peak indicate that there is only a weak hybridization between the europium vibrational mode at 7.3 meV and the small peak in the iron partial DOS at 9 meV. The peaks at 12.0 and 17.8 meV result from a small hybridization of the europium vibrations with the antimony vibrations as shown by the earlier calculations.[8,10]

The mean-force constants for the Eu and Fe atoms in the RFe_4Sb_{12} compounds have been obtained from the third moment of the measured probability of nuclear absorption and are given in Table I together with the fitted self-force constants reported in Table II of Ref. 10. The agreement between the Eu and La force constants is fair, whereas the agreement between the Fe measured and fitted force constants is good. The difference between the force constant for the rattler and iron predicted in the calculations[10] is certainly confirmed by the measurements. Finally, the temperature dependence of the Lamb-Mössbauer factor in $Ce^{57}Fe_4Sb_{12}$ agrees well with that previously observed[16] by iron-57 transmission Mössbauer spectroscopy.

Finally, our Eu-151 nuclear inelastic measurements on $EuFe_4Sb_{12}$ have proven insufficient to extract a reliable partial vibrational DOS at 295 K. This is fully understood in view of the 25-K results presented above. In Fig. 2 we compare the nuclear inelastic scattering spectrum measured at

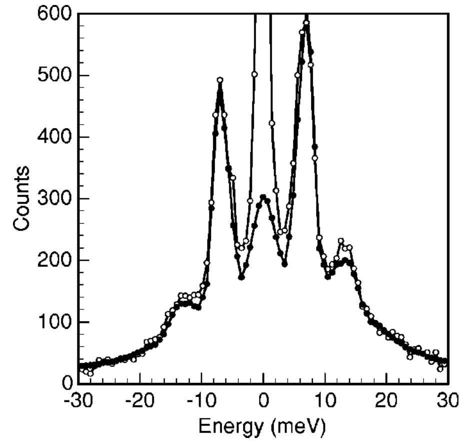

FIG. 2. The Eu-151 nuclear inelastic scattering of $EuFe_4Sb_{12}$ observed at 295 K (open circles) and calculated at 295 K from the 25-K DOS shown in Fig. 1(a) (closed circles). The spectra have been normalized on the peak at 7 meV and the experimental elastic peak at zero energy has been truncated.

295 K with the one calculated using the DOS obtained at 25 K [Fig. 1(a)]. The two spectra have been normalized at the maximum of the two peaks at ±7 meV and the full experimental elastic peak at zero energy has been truncated. It is clear that the observed energies and relative intensities of the different peaks are well reproduced by the 295-K calculated scattering pattern. The most striking feature of the calculated spectrum is the intense multiphonon contribution in the peak at zero energy. Undoubtedly it is this intense contribution which renders unreliable the extraction of the partial europium vibrational DOS from the 295-K scattering pattern. Hence, it is concluded that it is absolutely necessary to record data at low temperatures—here 25 K—to obtain the partial europium vibrational DOS in such a relatively soft system, where low-energy modes dominate. Such a behavior has already been observed[21] in the case of β tin.

IV. CONCLUSIONS

The europium partial vibrational DOS in $EuFe_4Sb_{12}$ and the iron partial DOS in $EuFe_4Sb_{12}$ and $Ce^{57}Fe_4Sb_{12}$ have been measured by nuclear inelastic scattering. These experimental results reveal the localized character of the europium vibrations at 7.3 meV, the strong decoupling of the iron and europium vibrations, the near independence of the iron partial DOS upon the nature of the rare-earth guest atom, the weak hybridization of the europium and antimony vibrational modes, and the temperature independence of the europium and iron partial DOS. The calculated[8,10,19] vibrational DOS in $LaFe_4Sb_{12}$ is in excellent agreement with our experimental measurements. Hence, nuclear inelastic scattering has proven to be a powerful method for the investigation of the lattice dynamics of the filled skutterudites, compounds for which this lattice dynamics is of high importance in determining the thermoelectric properties. Our work opens the way to the study of other, even more complex, materials, such as the europium-filled clathrates[22–24]—another family of compounds with potential thermoelectric applications.

The results reported herein indicate that the dynamics of the rattling atom is strongly decoupled from the iron-antimony framework, however, the definitive proof of this decoupling will require an experimental determination of the antimony partial DOS. To date, the rattler dynamics emerges essentially as a harmonic picture, in agreement with theoretical calculations.[8] The filled skutterudites probably provide the best example of localized independent vibrational modes and are a clear illustration of the concept of the Einstein oscillator developed in an historical paper[25] on the quantum theory of solids.

However, the above harmonic picture raises the important question of how the addition of an atom that interacts with the lattice in an essentially harmonic fashion yields as significant a reduction in the lattice thermal conductivity as has been observed.[4,7] A theoretical investigation[5] has indicated that the additional scattering by resonant rattlers in the cages of a filled clathrate yields a reduction in the thermal conductivity of one order of magnitude with respect to the analogous unfilled clathrate. The question of how the observed harmonic picture of the rattler in filled skutterudites is to be reconciled with a strong scattering of the acoustic phonons is still an unanswered question. A possible mechanism known as the "resonant scattering" has been proposed.[26] The absorption of phonons into the low-energy localized vibrational modes may, to some extent, trap a small amount of the vibrational energy in an excited "rattler" state, an energy that can then decay into phonons with k vectors incoherently related to the k vector of the absorbed phonons. This "resonant scattering" mechanism would lead to a significant reduction in the thermal conductivity even in the presence of weak anharmonic interactions. Unfortunately, at this point, the experimental verification of this proposal is not straightforward.

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