Lattice dynamics in the FeSb$_3$ skutterudite


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Thin films of FeSb$_3$ were characterized by electronic transport, magnetometry, x-ray diffraction, $^{57}$Fe and $^{121}$Sb nuclear inelastic scattering, and $^{57}$Fe Mössbauer spectroscopy. Resistivity and magnetometry measurements reveal semiconducting behavior with a 16.3(4) meV band gap and an effective paramagnetic moment of 0.57(6) $\mu_B$, respectively. A systematic comparison of the lattice dynamics with CoSb$_3$ and EuFe$_2$Sb$_2$ reveals that the Fe$_2$Sb$_2$ framework is softer than the Co$_2$Sb$_2$ framework, and that the observed softening and the associated lowering of the lattice thermal conductivity in the RFe$_2$Sb$_2$ filled skutterudites is not only related to the filler but also to the Fe$_2$Sb$_2$ framework.

I. INTRODUCTION

Skutterudites are promising thermoelectric materials that have been intensively studied since the 1990s. They possess interesting semiconducting properties, notably a large Seebeck coefficient, and a relatively low thermal conductivity that has been ascribed to the dynamics of the filler. In particular, the lattice dynamics of filled and unfilled skutterudites has been the object of intensive research. The semiconducting, magnetic, and thermal properties of the filled R(Fe,Co)$_4$Sb$_{12}$ skutterudites can be tuned by filling the (Fe,Co)$_4$Sb$_{12}$ framework with monovalent ions (e.g., Na$^+$ and Tl$^+$), divalent ions (e.g., Yb$^{2+}$ and Eu$^{2+}$), or trivalent ions (e.g., La$^{3+}$ and Ce$^{3+}$). However, only a limited degree of filling can be achieved in CoSb$_3$. In order to achieve larger degrees of filling, either Co must be substituted by Fe or a synthesis involving ball milling and subsequent hot pressing must be used.

Because there is no successful bulk synthesis procedure, the influence of filling the FeSb$_3$ structure on its lattice dynamics has been studied using different approaches. The direct comparison with the lattice dynamics of the Fe$_2$Sb$_2$ polyanion is not possible, thus one approach is the comparison of the lattice dynamics of the filled structures mentioned above with the related unfilled CoSb$_3$. Another approach is the study of the contribution of the filler to the density of phonon states (DPS). Density functional theory calculations of the partial density of phonon states have been carried out and compared with experimental data obtained by inelastic neutron scattering and nuclear inelastic scattering. The partial contributions to the DPS can also be investigated by ab initio powder-averaged lattice dynamic calculations and a subsequent comparison with inelastic neutron scattering measurements.

The synthesis of FeSb$_3$ is, however, possible by nanoscopy and this approach has recently been improved and now yields higher sample purity, but still produces only small amounts in the form of micrometer-thick films. Because detailed knowledge of the lattice dynamics in skutterudites is necessary to unravel the mechanisms that yield their low thermal conductivity, characterization methods suitable for thin films have to be used. Although inelastic neutron scattering experiments are in principle feasible, the beam time required would be prohibitively long because of the small amount of sample. In contrast, nuclear inelastic scattering (NIS) is a method of choice that yields the DPS for selected elements even with small samples. This method has been applied to the $^{57}$Fe nuclear resonance for some time, and has recently been developed for the $^{121}$Sb resonance. The resolution for the latter isotope was recently improved to $\sim$1.3 meV full width at half maximum (FWHM). It is thus possible to fully access the element-specific DPS in FeSb$_3$ and to obtain several related quantities, such as the mean force constants, the atomic displacement parameters, and the average velocity of sound.

Herein we report both the macroscopic characterization of high-purity FeSb$_3$ using resistivity and susceptibility measurements, and the microscopic characterization using synchrotron radiation diffraction, $^{57}$Fe Mössbauer spectral measurements, and nuclear inelastic scattering by $^{57}$Fe and $^{121}$Sb. A comparison of these results with the properties of CoSb$_3$ reveals that FeSb$_3$ is significantly softer, which is an observation that both indicates a combined influence of the filler and the substitution of Fe for Co on the lattice dynamics and hence thermal properties, and provides additional clues to the low thermal conductivity in filled skutterudites.

II. EXPERIMENT

The FeSb$_3$ thin films were deposited on Kapton foil at ambient temperature by the elemental modulated reactant method in a custom-built, ultra-high vacuum deposition system described elsewhere. Fe was deposited using a 3 kW electron-beam gun at a rate of 0.4 A/s, and Sb was deposited using an effusion cell at a rate of 0.6 A/s. A computer was used to control the deposition procedure. A quartz-crystal monitoring system placed 25 cm above each source was used to monitor the deposition process.
control the elemental layer modulation, the deposition rates, the shutter opening time for Fe, and the thickness for Sb. The precursors for the crystallized films were prepared by depositing multiple alternate layers of Fe and Sb until the desired film thickness was obtained. Deposition parameters were determined to yield the appropriate molar stoichiometry of FeSb3. These precursor films were then annealed under a nitrogen atmosphere at 410 K to form FeSb3. With this method, two films of thicknesses of ~1 and ~1.5 \( \mu \text{m} \) were deposited on a 25-\( \mu \text{m} \)-thick Kapton substrate. All further measurements were carried out on these two films.

Temperature-dependent resistivity and magnetization measurements were carried out between 10 and 300 K on a Quantum Design physical-properties measurement system (QD-PPMS) with the resistivity and the vibrating sample magnetometer options. The resistivity was measured on several 1-\( \mu \text{m} \)-thick samples with 2 by 5 mm\(^2\) lateral dimensions and different microcrack structures using the four-point method. The magnetization measurements were carried out with an applied magnetic induction of 0.25 T on a wrapped ribbon of the 1-\( \mu \text{m} \)-thick film that was 80 cm by 3.7 mm, i.e., ~12.9 mg of FeSb3. Hysteresis measurements have been carried out at 300 K up to 1.5 T in order to assess the presence of impurity phases and the diamagnetic contribution to the susceptibility. The same measurements have been carried out on polycrystalline CoSb3 for comparison. The susceptibility \( \chi \) was calculated from the magnetization by assuming the validity of the low field limit approximation \( \chi = M/H \), where \( M \) is the magnetization and \( H \) is the applied field.

Temperature-dependent x-ray diffraction (XRD) measurements were carried out at the 6-ID-D high-energy station at the Advanced Photon Source between 10 and 300 K. The x-ray wavelength was 0.124269 \( \text{\AA} \), and the sample-area detector distance was 1601.1(1) mm, as determined with a NIST SRM640c Si standard. Silicon (Chempur, 99.999%) was used as an internal standard for the temperature calibration. The sample contained ten layers of a ~1.5-\( \mu \text{m} \)-thick film of FeSb3 on Kapton foil and, for better thermal coupling to the sample holder, Al foil was placed between each layer. The powder-diffraction pattern of CoSb3 was measured under the same conditions. The data were reduced to diffractograms by using FIT2D\(^{24} \) and analyzed using the Rietveld method.\(^{25} \)

The \( ^{57}\text{Fe} \) Mössbauer spectra have been measured between 4.2 and 295 K on a constant-acceleration spectrometer that utilized a 295 K rhodium-matrix \( ^{57}\text{Co} \) source and was calibrated at 295 K with \( \alpha\text{-Fe} \) powder.

The \( ^{121}\text{Sb} \) NIS by FeSb3 was measured at the ID22N station at the European Synchrotron Radiation Facility (ESRF) operating in 16-bunch mode. A resolution of 1.3 meV was achieved by using a high-resolution backscattering monochromator with the (8 16 24 40) reflection of a sapphire single crystal cooled to ~237 K. The sample containing six layers of a ~1.5-\( \mu \text{m} \)-thick film of FeSb3 on Kapton foil with Al foil between each layer was cooled to 25 K in order to minimize multiphonon scattering. The \( ^{121}\text{Sb} \) NIS of CoSb3 and EuFe3Sb12 was measured on powder samples with the same setup and resolution. The 295 K \( ^{57}\text{Fe} \) NIS on the same FeSb3 sample was measured at the ID18 station at the ESRF operating in 16-bunch mode with a resolution of 0.7 meV.

III. RESULTS AND DISCUSSION

A. Electric transport and magnetism

Above ~40 K, the electrical resistivity \( \rho_{el} \) of FeSb3 decreases with increasing temperature (see Fig. 1), a decrease that is indicative of semiconducting behavior. A fit of the data in the high-temperature region (see inset in Fig. 1) with \(^{26}\)

\[ \rho_{el}(T) = A]\exp\left(\frac{E_g}{2k_B T}\right) \]

where \( E_g \) is the energy gap, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( A \) is a proportionality constant, yields an electronic band gap of 16.3(4) meV, which is a narrower gap than the 50 meV gap obtained by resistivity measurements\(^{20} \) on lightly \( p \)-doped CoSb3. As expected for rather thin films, the microstructure was found to be very important and resistivity measurements were carried out on several samples. The smallest cracks or scratches increase the resistivity by several orders of magnitude with respect to pristine samples. Further, heating the sample above 300 K (not shown) induces additional microstructure and increases the resistivity because of the differential thermal expansion between Kapton and FeSb3. Atomic-force microscopy measurements were carried out to monitor this behavior and to assure that the results in Fig. 1 were obtained on a sample free of cracks at the ~50 nm level. Such a dependence of the resistivity on the microstructure has also been observed\(^{27} \) in polycrystalline CoSb3, with reported resistivities of undoped samples between 7 and 1000 \( \mu \Omega \text{cm} \) at room temperature.\(^{27–33} \) The 300 K resistivity of 29.4(1) \( \mu \Omega \) m observed for crack-free FeSb3 is similar to the 37 \( \mu \Omega \) m of a polycrystalline, sintered, CoSb3 sample,\(^{30} \) which also exhibits the temperature dependence of a typical semiconductor.

The molar susceptibilities \( \chi_{m} \) of FeSb3 and CoSb3 are shown in Fig. 2. First, the diamagnetic contribution was obtained from the slope of a hysteresis loop measurement at 300 K (see Fig. 3) and associated with the sample holder, the ion core diamagnetism, and, for the FeSb3 films, with the Kapton substrate. The resulting corrections of \( \chi_{m}^{dia} \) were assumed to be temperature independent and were used to obtain the results shown in Fig. 2. Second, a small amount of soft ferromagnetic impurity in FeSb3 was observed in the hysteresis...
loop (see Fig. 3), and this contribution was subtracted. The magnetization of this impurity is essentially saturated at 0.25 T. Finally, a small correction term $\chi_0$, amounting to $\sim 12\%$ of the diamagnetic correction, was added to account for imperfections in the correction procedure. Adding $\chi_0$ immediately yielded paramagnetic Curie-Weiss behavior for FeSb$_3$ between 70 and 300 K. A plot of $1/\chi_m$ (see Fig. 2) yields a Curie constant of 0.520(2) cm$^3$/K/mol with a Curie-Weiss temperature of 0 K. The inset of Fig. 2 indicates that the effective paramagnetic moment of FeSb$_3$ of 0.57(6) $\mu_B$/f.u. was obtained, a value that is compatible with earlier reports.$^{33}$

A study of Co$_{1-x}$Fe$_x$Sb$_3$, with x ranging from 0 to 0.1, has shown that $\mu_{eff}$ increases with increasing Fe content up to a maximum of 1.7 $\mu_B$/f.u., a value that could correspond$^{32}$ to low-spin Fe$^{3+}$. This behavior obviously does not extrapolate to FeSb$_3$, which exhibits a much smaller effective paramagnetic moment.

From the $y$-axis intercept of the magnetic hysteresis loop in Fig. 3, an impurity phase of 0.004(1) at. % was obtained by assuming a typical mean value of 2.2 $\mu_B$ per Fe impurity atom at room temperature. The coercive field of $\sim 80$ Oe indicates that the impurity phase is not elemental Fe. For CoSb$_3$, an elemental Co impurity phase of 0.0005(2) at. % was obtained using the same procedure.

### B. X-ray diffraction

X-ray diffraction (see Fig. 4) indicates$^{18,34}$ that both FeSb$_3$ and CoSb$_3$ form a cubic lattice with space group $Im\overline{3}$ (No. 204) and have the skutterudite structure (see Fig. 5), where Fe or Co and Sb are located on the 8$c$ and 24$g$ sites, respectively. The inset to Fig. 4 shows the detector image with homogeneous Debye-Scherrer rings that indicate the absence of texture. Apart from the Si internal standard, small traces of an impurity are observed as a shoulder at $2\theta \sim 2.3^\circ$ in Fig. 4, indicating a polycrystalline Sb impurity of less than 3 wt. %. No further phases or Al thermalization layers are observed. Because of the large background resulting from the ten layers of Kapton foil, the Fourier filtering option was used to properly subtract the background, however, even with this option, the data below $2\theta = 2.1^\circ$ cannot be refined because the background is too large and not monotonous.

### TABLE I. Rietveld refinement parameters for FeSb$_3$ and CoSb$_3$.

<table>
<thead>
<tr>
<th></th>
<th>FeSb$_3$ (10 K)</th>
<th>FeSb$_3$ (300 K)</th>
<th>CoSb$_3$ (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_f$ (%)</td>
<td>6.5</td>
<td>6.5</td>
<td>5</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>9.2116(6)</td>
<td>9.2383(6)</td>
<td>9.0320(8)</td>
</tr>
<tr>
<td>$\gamma$ Sb</td>
<td>0.3402(2)</td>
<td>0.3399(3)</td>
<td>0.3356(3)</td>
</tr>
<tr>
<td>$\alpha$ Sb</td>
<td>0.1578(2)</td>
<td>0.1573(3)</td>
<td>0.1586(3)</td>
</tr>
<tr>
<td>Sb occupation (%)</td>
<td>0.96(1)$^a$</td>
<td>0.96(1)$^a$</td>
<td>0.99(1)$^a$</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>7.157(1)</td>
<td>7.096(1)</td>
<td>7.648(1)</td>
</tr>
<tr>
<td>$(\mu^2)$ Sb (Å$^2$)</td>
<td>0.028(1)</td>
<td>0.034(1)</td>
<td>0.004(1)</td>
</tr>
<tr>
<td>$(\mu^2)$ Fe/Co (Å$^2$)</td>
<td>0.010(3)</td>
<td>0.013(3)</td>
<td>0.011(3)</td>
</tr>
</tbody>
</table>

$^a$constrained to the 10 K value.
The thermal expansion calculated from the temperature dependence of the lattice parameters is shown in Fig. 6. In order to reduce noise in the data, especially at low temperatures, the temperature dependence of the lattice parameters was first modeled with a third-order polynomial function \( a_m(T) \); see the fit lines at the top of Fig. 6. The differences between the fitted curve and the data were less than \( 4 \times 10^{-4} \) Å. The thermal expansion coefficient \( \alpha \) was then obtained from the derivative, \( \alpha = \frac{d a_m(T)/dT}{a_m(300 \text{ K})} \). The absolute values for the Sb mean-square displacements are not reliable because they are too large for FeSb3, whereas for CoSb3, they are too small with respect to an expected value of \( \sim 0.01 \) Å\(^2\) at 300 K; see Sec. III D. The likely reason for this discrepancy is that the \( 2\theta \) range of the measurement was too narrow. Nevertheless, the temperature dependence of the mean-square displacements is reasonable. From the slope, \( d\langle u^2 \rangle/dT = 3\hbar^2/(m k_B \theta_D^2) \), where \( m \) is the mass of Sb, Fe, or Co, fitted between 100 and 300 K, Debye temperatures \( \theta_D \) of 230(5) and 410(10) K for Sb and Fe, respectively, have been obtained for FeSb3. The average value of the Debye temperature in FeSb3, calculated from \( \theta_D^v = (3\theta_D,\text{Sb} + \theta_D,\text{Fe})/4 \), is 275(5) K. In CoSb3, the Debye temperatures of 280(10) and 380(30) K for Sb and Fe, respectively, have been obtained, and \( \theta_D^v = 305(15) \) K is larger than in FeSb3; the average value is in good agreement with the literature value\(^{39} \) of 307 K obtained from the heat capacity of CoSb3.

Sb is located on a general \((0, y, z)\) position and the \( y \) and \( z \) positions have been refined. \( y + z = 0.4972(6) \) and 0.4942(6) for FeSb3 and CoSb3, respectively. FeSb3 more closely fulfills the Oftedal relation\(^{40} \) \( y + z = 1/2 \), which indicates that the rectangular Sb rings (see Fig. 5) are closer to squares in FeSb3 than in CoSb3.

C. Mössbauer spectroscopy

The 4.2 and 295 K\(^{57}\)Fe Mössbauer spectra of the \( \sim 1.5 \) μm film of FeSb3 are shown in the upper panel of Fig. 7; the spectra...
The errors are estimated to be 0.005 mm/s for the isomer shift δ, quadrupole splitting $\Delta E_Q$, and linewidth $\Gamma$, and 0.005% ε (mm/s) for the absorption area.

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>$T$ (K)</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E_Q$ (mm/s)</th>
<th>$\Gamma$ (mm/s)</th>
<th>Total area (%ε) (mm/s)</th>
</tr>
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<tr>
<td>1</td>
<td>295</td>
<td>0.390</td>
<td>0.338</td>
<td>0.297</td>
<td>1.668</td>
</tr>
<tr>
<td>225</td>
<td>0.432</td>
<td>0.350</td>
<td>0.302</td>
<td>1.798</td>
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<tr>
<td>155</td>
<td>0.463</td>
<td>0.363</td>
<td>0.307</td>
<td>1.917</td>
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</tr>
<tr>
<td>85</td>
<td>0.490</td>
<td>0.373</td>
<td>0.309</td>
<td>2.029</td>
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<tr>
<td>60</td>
<td>0.491</td>
<td>0.379</td>
<td>0.306</td>
<td>2.037</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.494</td>
<td>0.375</td>
<td>0.306</td>
<td>2.040</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>0.493</td>
<td>0.375</td>
<td>0.315</td>
<td>2.070</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>295</td>
<td>0.389</td>
<td>0.333</td>
<td>0.276</td>
<td>2.808</td>
</tr>
<tr>
<td>225</td>
<td>0.432</td>
<td>0.347</td>
<td>0.293</td>
<td>3.045</td>
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<tr>
<td>155</td>
<td>0.465</td>
<td>0.366</td>
<td>0.309</td>
<td>3.266</td>
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<tr>
<td>85</td>
<td>0.490</td>
<td>0.373</td>
<td>0.312</td>
<td>3.471</td>
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<tr>
<td>60</td>
<td>0.489</td>
<td>0.375</td>
<td>0.303</td>
<td>3.526</td>
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</tr>
<tr>
<td>40</td>
<td>0.493</td>
<td>0.373</td>
<td>0.312</td>
<td>3.577</td>
<td></td>
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<tr>
<td>4.2</td>
<td>0.493</td>
<td>0.375</td>
<td>0.312</td>
<td>3.564</td>
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</table>

The isomer shifts are given relative to 295 K α-Fe powder.

obtained for both films and at intermediate temperatures are very similar. In addition to the diffraction measurements that revealed no crystalline impurity phase, no further amorphous iron-bearing impurity is observed. All measured spectra were fitted with a simple symmetric quadrupole doublet with two Lorentzian line shapes, with parameters given in Table II. The Mössbauer spectra show no convincing evidence for a second component related to Fe with missing Sb near neighbors, as would be expected from the hypothetical partial Sb occupancy seen in the diffraction measurements. The 96(1)% Sb occupancy (see Table I) would imply that more than 20% of the Fe have less than six Sb near neighbors, which would be visible in the Mössbauer spectra. The temperature dependence of the isomer shift δ, quadrupole splitting $\Delta E_Q$, linewidth $\Gamma$, and the recoil-free fraction $f_{\text{LM}}$ are shown in the lower panel of Fig. 7. The temperature dependence of δ and $f_{\text{LM}}$ have been fit with a Debye model for a solid.

The temperature dependence of the isomer shift is well fit with the Debye model for the second-order Doppler shift with a characteristic Mössbauer temperature $\theta_M$ of 541(10) and 530(10) K for the ∼1.5 and ∼1 μm films, respectively. This temperature is much larger than the Debye temperature $\theta_{D,\text{Fe}}$ of 350(5) and 373(6) K of the ∼1.5 and ∼1 μm films, respectively, obtained from the temperature dependence of the logarithm of the spectral absorption area $f_{\text{LM}}$. The latter values are in good agreement with the values obtained herein by other techniques; see Table III. It is known that the two temperatures $\theta_M$ and $\theta_{D,\text{Fe}}$ obtained from the two temperature dependencies, are usually different because they depend, for the isomer shift, on $\langle v^2 \rangle$, which is the mean-square vibrational velocity of the $^{57}\text{Fe}$, and, for the absorption area, on $\langle \mu^2 \rangle$, which is the mean-square atomic displacement of the $^{57}\text{Fe}$; there is no model-independent relationship between these mean-square values. However, measurements of the Mössbauer temperatures on various compounds indicate that $\theta_M$ is often twice as large as $\theta_{D,\text{Fe}}$, i.e., the isomer shift is more sensitive to higher-energy phonons.

The Fe DPS of FeSb$_3$ (see below) clearly reveals that the Fe vibrations have a strong non-Debye behavior and are dominated by two strong optical modes above 30 meV. Because we have measured the partial DPS $g(E)$ by $^{57}\text{Fe}$ NIS (see

<table>
<thead>
<tr>
<th>Technique</th>
<th>$\theta_{D,\text{Fe}}(K)$</th>
<th>$\theta_{D,\text{Sb}}(K)$</th>
<th>$\theta_{D,\text{Co}}(K)$</th>
<th>$\theta_{D,\text{Fe}}(K)$</th>
<th>$\theta_{D,\text{Co}}(K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle v^2 \rangle$, XRD</td>
<td>230(5)</td>
<td>410(10)</td>
<td>275(5)$^a$</td>
<td>280(10)</td>
<td>380(30)</td>
</tr>
<tr>
<td>Mössbauer spectral area 1.5 μm</td>
<td>350(5)</td>
<td>430(10)</td>
<td>240(10)</td>
<td>250(5)</td>
<td>410(10)$^b$</td>
</tr>
<tr>
<td>Heat capacity DPS</td>
<td>210(5)</td>
<td>370(5)</td>
<td>255(5)$^a$</td>
<td>245(5)</td>
<td>360(10)$^b$</td>
</tr>
<tr>
<td>Heat capacity macroscopic $\theta_D$ from $v_s$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_s$,$\text{Sb}$</td>
<td>$v_s$,$\text{Fe}$</td>
<td>$v_s$,$\text{Co}$</td>
<td>$v_s$,$\text{Sb}$</td>
<td>$v_s$,$\text{Co}$</td>
<td></td>
</tr>
<tr>
<td>Pulse echo</td>
<td>2400(100)</td>
<td>2390(10)</td>
<td>2600(100)</td>
<td>2930$^d$</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Technique</th>
<th>$F_{\text{Sb}}^w$ (N/m)</th>
<th>$F_{\text{Fe}}^w$ (N/m)</th>
<th>$F_{\text{Sb}}^w$ (N/m)</th>
<th>$F_{\text{Co}}^w$ (N/m)</th>
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<tr>
<td>NIS</td>
<td>105(5)</td>
<td>186(1)</td>
<td>160(10)</td>
<td>119$^b$</td>
</tr>
</tbody>
</table>

$^a$obtained from $\theta_{\gamma} = [3\theta_{D,\text{Sb}} + \theta_{D,\text{Fe/Co}}]/4$.

$^b$obtained from Ref. 16.

$^c$obtained from Ref. 39.

$^d$obtained from Ref. 28.
FIG. 7. (Color online) Top: The Mössbauer spectra of FeSb₃ obtained on a 1.5 μm film. Bottom: The fit parameters obtained from the spectra of the ~1 and ~1.5 μm films (open and closed symbols), respectively. The errors are the size of the symbols. The crossed square indicates the $f_{LM}$ obtained directly from the $^{57}$Fe NIS at 295 K. The dashed line indicates the second-order Doppler shift obtained from the DPS; see text. The lines for the Doppler shift and $f_{LM}$ are Debye model fits. The lines for $\Delta E_Q$ and $\Gamma$ are quadratic polynomial fits given as a guide for the eye.

below), we can directly obtain the second-order Doppler shift\(^\text{42}\)
\[
\delta_{\text{SOD}}(E) = -\langle v^2 \rangle / (2c)
\]
from the average kinetic energy\(^\text{20}\)
\[
\langle E_{\text{kin}} \rangle = 1/2m_R \langle v^2 \rangle = 3/4 \int_0^{\infty} \text{coth}(E/(2k_B T)) g(E)E dE,
\]
where $m_R$ is the mass of the resonant nucleus. The obtained temperature dependence of the isomer shift with the second-order Doppler correction is shown in Fig. 7, and corresponds to $\theta_M = 440$ K. The difference is thus only partly explained and other corrections such as thermal expansion, which modifies the DPS and therefore $\langle E_{\text{kin}} \rangle$, or the influence of charge carrier activation on the isomer shift, might be necessary.

D. Nuclear resonance scattering

The nuclear inelastic scattering spectra from the $^{121}$Sb NIS measurements in FeSb₃, CoSb₃, and EuFe₄Sb₁₂ are shown in Fig. 8, together with the instrumental functions measured by nuclear forward scattering. The resolution of the instrument was ~1.3 meV for all measurements. $^{121}$Sb NIS measurements on the latter two compounds have been published previously\(^\text{17}\) with a resolution of 4.5 meV. The measurements have been repeated because of the enhanced resolution.\(^\text{22}\) After subtraction of the elastic peak, the extraction of the DPS has been performed by the conventional procedure, i.e., the correction of the multi-phonon contribution of the Fourier transformation of the inelastic scattering, which was slightly modified in order to take into account the asymmetry of the instrumental function; the data were deconvoluted by the experimental instrumental function and convoluted with a symmetric Gaussian with a FWHM of 1.7 meV, which is a value slightly larger than the ~1.3 meV resolution that was chosen in order to avoid unphysical termination ripples in the DPS. The validity of the procedure was confirmed by applying the usual sum rules.\(^\text{45}\) The $^{57}$Fe NIS spectrum of FeSb₃ measured at 295 K is also shown in Fig. 8. The instrumental
FIG. 9. (Color online) Comparison of the DPS measured with the $^{57}$Fe resonance at 295 K for FeSb$_3$ and EuFe$_4$Sb$_{12}$ (top) and with the $^{121}$Sb resonance at 25 K for FeSb$_3$, CoSb$_3$, and EuFe$_4$Sb$_{12}$ (bottom). The insets show the reduced partial DPS $g(E)/E^2$ in units of $10^{-4}$/meV$^3$, and the low-energy fit between 0 and 4 meV for the Debye levels, indicated by the same type of lines. The differences in the Debye levels for Fe and Sb in FeSb$_3$ and EuFe$_4$Sb$_{12}$ are due to the different masses of the elements; see Eq. (1).

resolution was 0.7 meV and the DPS was obtained by the conventional procedure.$^{44}$ After the multiphonon correction, the partial DPS $g(E)$ were obtained (see Fig. 9), which also shows the $^{57}$Fe DPS of EuFe$_4$Sb$_{12}$ from Ref. 46. The Fe DPS consists of two small broad peaks at $\sim$7 and 15 meV and a large broad peak around 30 meV. The latter broad peak is split and corresponds to a somewhat softer phonon mode in the EuFe$_4$Sb$_{12}$ filled skutterudite. The splitting of this peak was also observed in the LaFe$_4$Sb$_{12}$ filled skutterudite using inelastic neutron scattering measurements,$^{16}$ and in CeFe$_4$Sb$_{12}$ using NIS.$^{46}$ The low-energy portion of the DPS indicates that FeSb$_3$ is softer than EuFe$_4$Sb$_{12}$, as seen from the large increase in the reduced DPS $g(E)/E^2$; see insets to Fig. 9. The Sb vibrations mainly appear below 25 meV, but a small contribution of the Sb vibrations is also observed around 30 meV. The latter part of the DPS is not well resolved due to the multiphonon contributions in the experimental data. By comparing the partial DPS in different compounds, we observe that the Sb DPS in CoSb$_3$ exhibits pronounced features, such as gaps at 12 and 21 meV, and a well-resolved peak at 23 meV. Inelastic neutron scattering measurements have also revealed$^{16}$ this better resolution of the individual peaks in CoSb$_3$ as compared with $R$Fe$_4$Sb$_{12}$. However, this difference is not directly related to the filling of the skutterudites, because the DPS of FeSb$_3$ shows the same broad features as EuFe$_4$Sb$_{12}$. The most pronounced difference of the DPS in FeSb$_3$ as compared to other filled and unfilled skutterudites is an overall softening of the phonon modes, which leads to an enhancement of the DPS between 5 and 10 meV. This softening, which is also observed in the Fe DPS in FeSb$_3$ at low energies (see Fig. 9) indicates a lower velocity of sound and might be crucial in determining the thermal conductivity and, therefore, the thermoelectric properties of skutterudites. In EuFe$_4$Sb$_{12}$, the essentially single frequency and Einstein-like DPS of the Eu filler appears$^{46}$ at $\sim$7 meV. The relative hardening of the Sb DPS between FeSb$_3$ and EuFe$_4$Sb$_{12}$, seen in the lower DPS of EuFe$_4$Sb$_{12}$ at $\sim$7 meV, might be related to the appearance of this filler mode. Calculations of the lattice dynamics in FeSb$_3$ would thus be highly desirable in order to confirm this hypothesis.

Several thermodynamic and vibrational quantities can be obtained from the DPS.$^{20}$ The element-specific heat capacity $C_V$ can be directly calculated from the DPS. The total heat capacity $C_V$ of FeSb$_3$ was obtained by combining the partial $C_V$ for Fe and Sb obtained from NIS by $C_V = 3C_Sb + C_{Fe}$, are shown in Fig. 10. These values are compared with the total $C_V$ of CoSb$_3$, obtained by combining the partial $C_V$ for Co obtained from calculations$^{16}$ and Sb from NIS measurements, which are measurements that are in good agreement with the calculation in Ref. 16. A macroscopic $C_p$ measurement of CoSb$_3$, carried out with the $C_p$ option of the QD-PPMS that is in excellent agreement with earlier results,$^{39}$ is also shown. With a Debye fit of the $C_V$ between 2 and 300 K, Debye temperatures for Sb and Fe in FeSb$_3$ of 210(5) and 430(10) K, respectively, have been obtained, values that are in good agreement with those obtained by diffraction; see Table III. From $C_V$ for FeSb$_3$, a Debye temperature of 240(10) K has been obtained. The partial $C_V$ of CoSb$_3$ yields Debye temperatures of 250(5) and 410(10) K for Sb and Co, respectively. The total Debye temperature of CoSb$_3$ from the macroscopic measurement is 280(10) K, which is compared with $R$Fe$_4$Sb$_{12}$. However, this difference is not directly related to the filling of the skutterudites, because the DPS of FeSb$_3$ shows the same broad features as EuFe$_4$Sb$_{12}$.
in good agreement with the $\theta_D = 285(10)$ K obtained from the combined experimental $^{121}$Sb NIS $C_V$ and the theoretical Co $C_V$.

From the Debye level $\lim_{E \to 0} [g(E)/E^2]$, obtained from the low-energy modes in the reduced DPS (see the insets to Fig. 9), the average velocity of sound $v_s$ of 2390(10) and 2790(10) m/s for FeSb$_3$ and EuFe$_4$Sb$_{12}$, respectively, was obtained from the $^{57}$Fe NIS using \[ \lim_{E \to 0} [g(E)/E^2] = \frac{m_g}{2\pi^2 \rho h v_s^2}, \]  
where $\rho$ is the density of the material and $m_g$ is the mass of the resonant nucleus. These velocities of sound are consistent with the Sb Debye level in FeSb$_3$ and EuFe$_4$Sb$_{12}$, as indicated by the dashed lines in the insets to Fig. 9; see also Table III. For CoSb$_3$, a $v_s$ of 2600(100) m/s is obtained from the Debye level, which is in fair agreement with the literature value of 2930 m/s. The large error arises from the imprecision in the Debye level obtained only from the $^{121}$Sb NIS. By using the low-temperature Debye approximation $v_s = (k_B \theta_D)/(\hbar(6\pi^2 N)^{1/3})$, with the density of atoms $N$, the low-temperature $\theta_D^{LT} = 245(5)$ K is obtained for FeSb$_3$, a value that is significantly lower than $\theta_D^{LT} = 307$ K reported for Co$_3$Sb$_4$.

The Lamb-Mössbauer factor $f_{LM}$ obtained from NIS provides access to the atomic mean-square displacements, $\langle u^2 \rangle = -\ln(f_{LM})/k^2$, where $k$ is the incident wave vector. In FeSb$_3$, the $f_{LM}^{SB}$ is 0.58(1) and $\langle u^2 \rangle$ is 0.0015(5) Å$^2$ for Sb at 25 K, and $f_{LM}^{SB}$ is 0.73(5) and $\langle u^2 \rangle$ is 0.0057(4) Å$^2$ for Fe at 295 K. These values are much smaller than the $\langle u^2 \rangle$ values obtained by diffraction. Note that the displacement parameter obtained by NIS is a purely incoherent one-particle displacement and is not affected by the site occupation or disorder, whereas the $\langle u^2 \rangle$ values obtained from diffraction sometimes are affected. The temperature dependence of $\langle u^2 \rangle$ obtained from the DPS is in agreement with the temperature dependence of $\langle u^2 \rangle$ obtained by diffraction, apart from an additive constant, which reflects either a static displacement, a site disorder, or an incomplete site occupation. The element-specific Debye temperatures can be calculated directly from $g(E)$ with the expression $\theta_D = 3/[k_B^2 \int_0^{E_d} g(E) E^2 dE]$ obtained in the high-temperature limit; see Ref. 20. For FeSb$_3$, Debye temperatures of 210(10) K for Sb and 370(5) K for Fe were obtained; the average value of 255(5) K is in agreement with 245(5) and 240(10) K obtained from sound velocity and $C_V$, respectively. The element-specific Debye temperature in CoSb$_3$ was obtained from the measured $^{121}$Sb DPS of 245(5) K, and from the theoretical Co DPS of 360(10) K. In order to provide an easy comparison between the results of the different methods, we give a summary of all the Debye temperatures in Table III. Arguably, the Debye temperature is a crude approximation, but allows straightforward comparison. In essence, we observe that the Sb sublattice is significantly softer in FeSb$_3$, whereas the Fe sublattice in FeSb$_3$ is harder than the Co sublattice in CoSb$_3$.

The DPS obtained from NIS also directly yields the element-specific mean force constants \[ F_m^{m} = m_g/h \int_0^{E_d} g(E) E^2 dE. \] The mean force constant of 160(10) N/m for Sb in CoSb$_3$ is larger than the values of 105(5) and 100(10) N/m observed for FeSb$_3$ and EuFe$_4$Sb$_{12}$, respectively, because the high-energy optical phonon modes of the filled structure are similar to FeSb$_3$, whereas in CoSb$_3$, they have a larger energy. The Sb force constant in CoSb$_3$ deviates from the literature value of 117 N/m obtained from earlier NIS measurements and from the mean force constant of Sb of 119 N/m obtained from calculations. This deviation can be ascribed essentially to the better resolution and more precise energy calibration available herein. Thus, the good agreement obtained earlier is not confirmed herein and the experimental mean force constant in CoSb$_3$ appears to be larger than the calculated value. The Sb mean force constant for EuFe$_4$Sb$_{12}$ is in good agreement with the $F_m^{m}$ obtained from previous NIS measurements. This indicates that by filling FeSb$_3$ with Eu, the average Sb binding does not change. Further, CoSb$_3$ has very different Sb lattice dynamics and thus is not an ideal compound for investigating the influence of filling upon the lattice dynamics of the $R$Fe$_4$Sb$_{12}$ compounds. In Fe$_3$Sb$_4$, the mean force constant is 186(1) N/m, which is a value close to the value of 190(4) N/m in EuFe$_4$Sb$_{12}$. The calculated mean force constant for Co in CoSb$_3$ of 176 N/m is slightly smaller, indicating a softer Co binding in the Co$_4$Sb$_{12}$ framework, as compared to the Fe binding in the Fe$_4$Sb$_{12}$ framework.

### IV. Conclusion

The magnetic and electric properties of FeSb$_3$ reveal semiconducting and paramagnetic behavior similar to CoSb$_3$, with, however, a larger effective paramagnetic moment. X-ray diffraction and Mössbauer spectral measurements reveal that the sample is very pure with at most 3 wt.% of elemental Sb as an impurity. Measurements of the lattice dynamics and the related quantities show that the Sb binding in FeSb$_3$ is significantly softer than in CoSb$_3$, whereas the Fe sublattice in FeSb$_3$ is harder compared to the Co sublattice in CoSb$_3$. The softening of the low-energy modes likely has a large influence on the thermal conductivity and thus favorably impacts the thermoelectric properties in FeSb$_3$. By filling the Fe$_4$Sb$_{12}$ framework, the low-energy optical phonon modes, which have mainly Sb character, shift to larger energies. The lattice dynamics in filled skutterudites depends both on the framework and the filler and, therefore, the Co$_4$Sb$_{12}$ framework is not ideal for the study of the influence of the filler on the lattice dynamics in $R$Fe$_4$Sb$_{12}$ skutterudites. It appears that for skutterudites, as was also suggested for clathrates, the role of the framework on the lattice dynamics should be revisited.

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