Dynamics of La and Ce filled xFe_4Sb_{12} skutterudite structures

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Abstract

We have applied high-resolution neutron time-of-flight spectroscopy and *ab initio* lattice dynamics calculations to study the guest dynamics of La and Ce in the filled skutterudite system xFe_4Sb_{12}. Both the experiments and the calculation show that the guest dynamics is governed by collective vibrations, i.e. phonons. Unlike the case of localized rattlers the guest modes reveal dispersive character and a non-trivial *Q*-dependence of the signal intensity. The rather low-energy of the guest modes is due to their higher mass and weaker bonding with the host network.

Introduction

Nanocage-based materials have been attracting a high scientific interest due to the wide range of potential industrial applications. For example, Zeolites are used for catalytical and filter processes [1], clathrate-hydrates are energy storing compounds [2], and clathrates and skutterudites are thought to be excellent thermoelectric materials [3,4].

In all these applications the dynamics of the host-lattice, of the intercalated guest atoms or molecules, and of the coupling between those two are crucial properties requiring a thorough understanding for improving their functionality. In particular the thermoelectric figure of merit of clathrates and skutterudites is often related to the coupling between the guest-atoms and the host-lattice. A rather common point of view on the low thermal conductivity of these systems is that the vibrations of the guests serve as decay channels for the heat-carrying phonons of the host-lattice [5,6]. This supposition is in agreement with the scenario proposed for the explanation of the low thermal conductivity of glasses.

Intuitively speaking this scenario requires a rather loose coupling of guest and host that does not preserve the phase of the vibrational modes. For this reason the guest dynamics is often referred to as localized mode, rattling mode, incoherent phonon, independent vibration, etc.

The experimental proof of the coupling scenario is a subtle task, since there are a number of physical and practical obstacles to overcome. First of all, the majority of the intercalated atoms and molecules has an appreciably higher mass *M* than the constituents of the host-network. Moreover, their bonding character with the lattice is of lower energy leading to smaller force constants *F*. Hence, the characteristic modes of the guests are shifted towards lower energies of some meV due to the relation $\omega \sim (F/M)^{1/2}$.

However, it should be noted that this relation applies equally to phonons, i.e. collective vibrations [7]. As a consequence, the observation of low-energy Einstein modes within the density of states of a filled nanocage compound does not allow to discriminate between supposed localized rattling modes of a guest and van Hove singularities of collective vibrations, hence, acoustic and optic phonons to which the guests contribute.

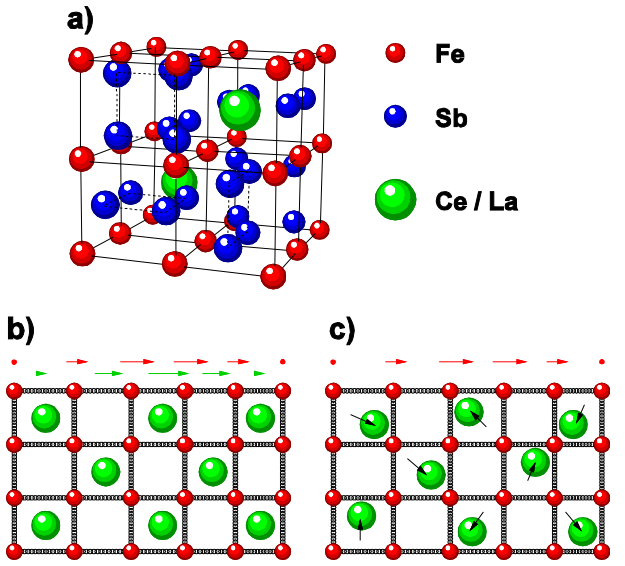

Figure 1: *a) 3-D sketch of the Ce/La positions in the bcc filled skutterudite structure. b) 2-D sketch of a collective mode preserving the phase relation between the guest atoms and between the guests and the host lattice. c) 2-D sketch of independent vibrations or rattling modes of the guests decoupled from the phonon mode of the host lattice. In both cases, half a period of the host lattice oscillation is sketched. Arrows indicate the displacement of the atoms.*

A disentangling of these two scenarios can only be achieved when experiments resolving not only energy but also spatial correlations are performed. In other words, one has to answer the question whether there is a well defined phase relation among the guests, and between the guests and the host lattice. Figures 1 b and c sketch the two scenarios of well correlated phonon processes and localized, independent vibrations of the encaged atoms, respectively.

For compounds with coherent nuclear scattering, like the ones we are dealing with, a comprehensive determination of the lattice dynamics of the system is conveniently carried out on single crystal samples in the four dimensional energy-momentum (ω-**Q**) phase. It is therefore unpractical for most of the nanocage compounds which are available as powders.

High resolution inelastic scattering needs to be done with rather low energy neutrons. In such experiments the phase space available is restricted and the standard incoherent approximation for obtaining the density of states is less reliable. However, it has been shown for the case of glasses, that independent localized modes have a stunningly simple relation between their intensity and modulus *Q* in scattering namely $I(Q) \sim Q^2$ [8,9]. This dependence is often referred to as quasi-incoherent scattering since it mimics the Q^2 response of purely incoherent systems although it may come from

coherently scattering atoms [10] (in neutron scattering experiments incoherence can be due to the nuclear spin and isotopic distribution of a particular atom species). In the case of coherent scattering the inelastic response is substantially modulated by the structure factor of the sample reflecting the spatial correlation between scattering sites and by the Eigenvectors of the atomic movements. Thus, for coherent scattering a Q^2 characteristic can only stem from the non-preservation of the phases of independent localized vibrations leading to a loss of information on the spatial correlations, and leaving the signal being exclusively due to self-correlation processes. As a clear consequence, any modulation of the $I(Q) \sim Q^2$ indicates a coupling between the guests and hosts and supports the scenario of low-energy collective modes. This offers us the opportunity of discriminating localized from collective vibrations by experiments. Furthermore, as it will be shown below, comparing our coherent neutron scattering results with calculations on powder averaged coherent response gives an additional handle for following up the microscopic nature of the lattice dynamics.

Neutron scattering experiments

Neutron time-of-flight (tof) spectroscopy is an excellent tool for studies of dynamics in powdered materials. Tof spectrometers map simultaneously a wide region of the ω-Q phase space, whose limits depend on the energy of incident neutrons and the coverage of the space with detectors [11].

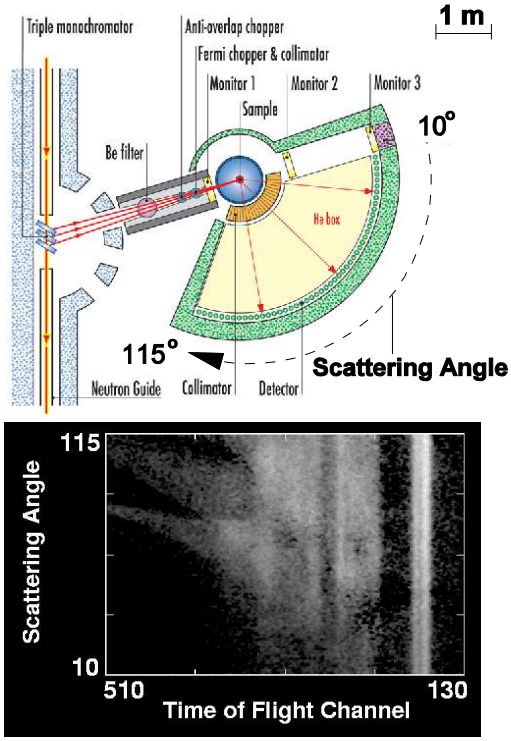

Figure 2: *Top, layout of the time-of-flight instrument IN6@ILL equipped with 337 detectors covering scattering angles between 10 and 115 degrees. Bottom, contrast plot of intensity of a $LaFe_4Sb_{12}$ sample plotted in natural units of the experiment, time-of-flight and scattering angle.*

Figure 2 shows a sketch of the tof spectrometer IN6@ILL stressing the wide range of scattering angles, i.e. Q numbers, covered by 337 detectors. The energy resolved signal of a $LaFe_4Sb_{12}$ sample measured with the IN6@ILL detector array is sketched at the bottom of Figure 2.

The IN6@ILL experiments have been performed with an incident neutron energy of 4.8 meV and T=300 and 600 K. We have utilized IN6 in the time-focusing mode, that allows to focus the best energy-resolution ΔE on the energy range of interest. In this case a ΔE=0.15 meV has been established at 6.5 meV the energy of the supposed Einstein oscillator. Thus, IN6 data are collected on the anti-Stokes line. For experiments at low T (2–150 K) the tof spectrometer IN4@ILL has been utilized offering an energy resolution on the Stokes line of 0.5 meV at an incident energy of 30 meV.

To establish the guest dynamics only we have applied the contrast method described before [12,13,14]. Due to almost identical masses Ce and La display the same Einstein mode energies. The scattering cross sections, however, differ by a factor of 3 between La and Ce offering a well approximated response of the guests only when applying difference functions to the inelastic response of the two samples.

Figure 3 reports the generalized density of states G(ω) of the La and Ce containing samples, as it is obtained in the incoherent approximation [14]. The G(ω) has been normalized to 51 modes corresponding with the number of normal modes of the 17 atoms in a unit cell. However, please note that the partial contributions to G(ω) as monitored by neutrons are weighed by the effective scattering power of the atoms determined by σ/M.

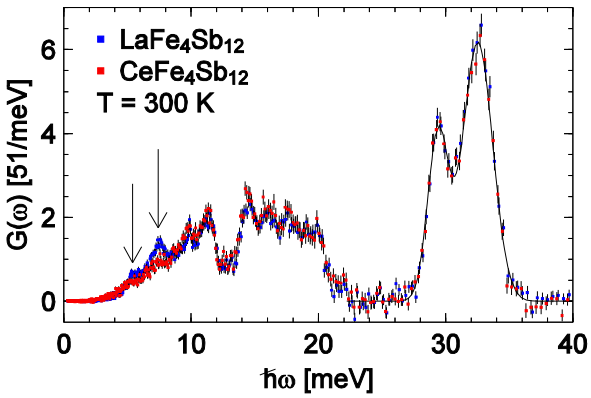

Figure 3: *The generalized density of states G(ω) of the La and Ce samples as measured at IN6@ILL at 300 K.*

It is obvious that the $G(\omega)$ of the two samples display identical features at energies above 9 meV. The two peaks at about 29.5 and 32.5 meV are due to Fe-modes. At energies between 9 and 22 meV the G(ω) is dominated by the inelastic response from the Sb atoms. Those findings have been established by lattice dynamics calculations [15,16,17] as well as neutron and x-ray experiments [13,14,17,18,19]. Maxima in the detailed structure of the Sb-band can be associated with Raman- and IR-active modes [16,20].

However, more interesting is the double peak feature at energies of 5.5 and 7.5 meV, both indicated by the vertical arrows in figure 3. Since these peaks are more pronounced in the La-sample, they are an unequivocal feature of the guest-dynamics. In contrast to prior experiments their visibility is due to the excellent energy resolution of 0.15 meV of the applied instrument. This double-peak has been as well observed in the high resolution mode at IN4@ILL down to

temperatures of 2 K. Within the energy resolution of the performed experiments it proved to be unaffected by *T* changes between 2 and 600 K, i.e. it is not governed appreciably by anharmonic effects.

Ab initio lattice dynamics calculations

To substantiate our experimental results we have equally performed *ab initio* lattice dynamics calculations using the codes VASP [21] and PHONON [22]. For comparison with the experimental powder average a random set of *Q* points has been generated in the spherical coordinate space and the inelastic response has been calculated by the direct method implemented in PHONON. In order to obtain a statistically representative average 1280000 *Q* points were generated and 300 energy points were calculated for each *Q* point. The phase space covered was that of the IN6@ILL spectrometer.

Figure 4 reports the inelastic signal calculated for the La contribution exclusively. On top the intensity is indicated on a linear scale stressing the strong intensity concentration around 7.5 meV. In a calculated *G(ω)* such an intensity concentration is associated with an Einstein-mode. However, a detailed inspection of data on a logarithmic scale, as it is done at the bottom of Figure 4, reveals a distribution of the inelastic signal over wide energy ranges. This feature indicates a pronounced coupling of the La dynamics to Sb and Fe modes.

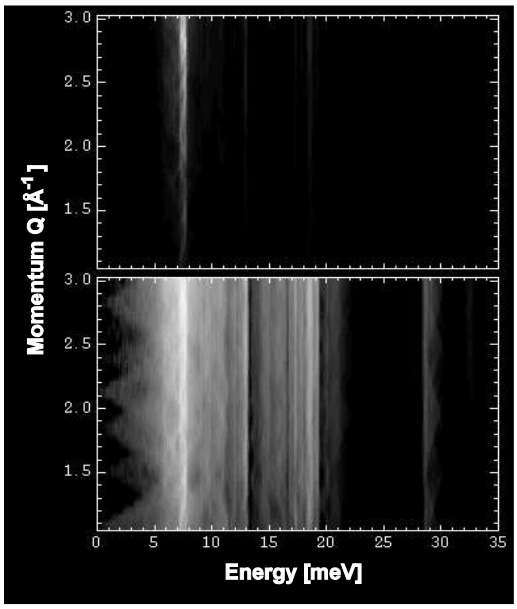

Figure 4: *Calculated inelastic contribution of La to the signal in the energy and momentum phase space. Top figure reports the intensity on a linear scale. Bottom figure reports the intensity on a logarithmic scale stressing the wide distribution of the La inelastic signal.*

Moreover, the dispersive intensity, in particular below 7.5 meV, gives evidence of the collective phonon behavior of La, as it is coupled to the Fe_4Sb_{12}-lattice. A dispersive character of phonons is as well observable at higher energies up to 30 meV, at which La couples apparently to the Fe modes.

This coupling can be as well visualized by computing the partial density of states from the lattice dynamics calculations. Figure 5 reports the total and the partial density of states. Our results are in full agreement with prior extensive lattice dynamics calculations [16,17]. It is in particular noteworthy that the profile of the La partial response below 8 meV is characterized by a double-maximum feature matching well with the experimentally determined results. This double-maximum is also present in the Sb partial density of states, though to a lower intensity, giving evidence of a common origin of the La and Sb modes and hence a coupling between the La and Sb dynamics.

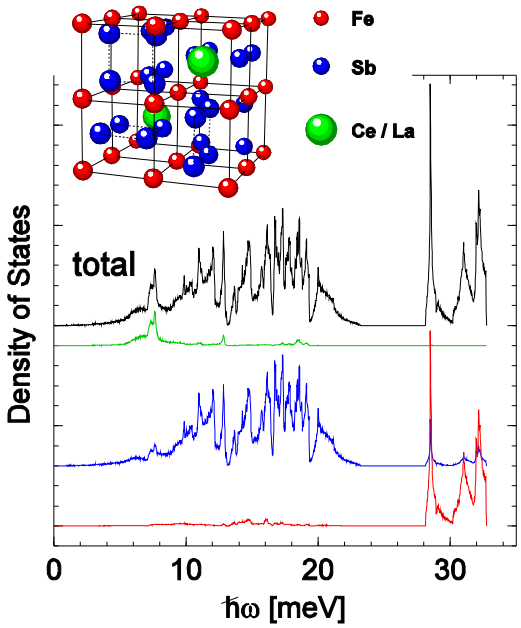

Figure 5: *Total and partial density of states as obtained from the ab initio lattice dynamics calculatios.*

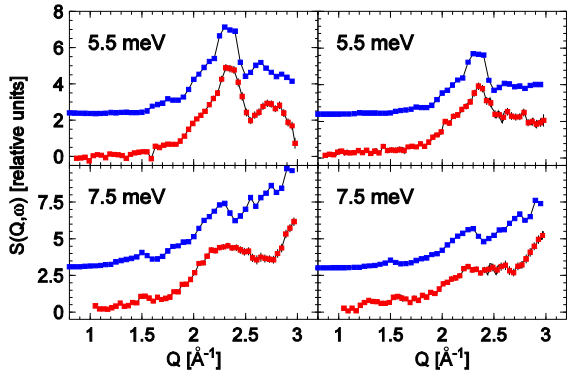

Figure 6: *Constant energy slices of the calculated (blue) and measured (red) inelastic intensity of $LaFe_4Sb_{12}$ (left) and $CeFe_4Sb_{12}$ (right) samples. Calculated data are shifted for clarity.*

To give a closer look at the *Q* dependence of the inelastic intensity, Figure 6 reports the signal from the neutron scattering experiments and as determined with the *ab initio* lattice dynamics calculation. For clarity we have chosen two constant energy slices only, namely 5.5 and 7.5 meV, and focus thus our interest on the double-maximum characteristic. Both signals, the measured and the calculated one, follow a detailed variation upon *Q* changes. This variation is highly pronounced in the case of $LaFe_4Sb_{12}$. This indicates that the La inelastic response is governed by collective phonon modes unlike the inelastic intensity of a localized, rattling guest-mode with a monotone Q^2 dependent intensity increase.

Conclusions

We have applied high-resolution neutron time-of-flight spectroscopy and *ab initio* lattice dynamics calculations to shed more light on the dynamics of the guest atoms in the filled skutterudite systems $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$. We have confirmed that the inelastic response of the guests is more complex than presented in prior studies in which spectroscopic techniques with a relaxed energy resolution of more than 1 meV were used. The vibrational density of states obtained as momentum averaged response in our experiments proved the existence of two Einstein modes centered around 5.5 and 7.5 meV, whose origin is the La/Ce guest dynamics.

Having inspected the Q-resolved signal in detail we can confirm a complex Q-dependence of the inelastic intensity pointing strongly at guest vibrations well correlated with the dynamics of the host lattice and, hence, preserving the phase of heat carrying phonons. Our lattice dynamics calculations support these findings and offer the picture of van Hove singularities of acoustic and optic phonons as the explanation for the two strong Einstein-modes in the response of the guest atoms.

In other words, the inelastic response of the filled skutterudite systems $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ is in agreement with a standard lattice dynamics scenario of a crystal. The shift of the guest modes towards low energies is due to the high mass of the encaged atoms and lower force constants working on them. The reduction in thermal conductivity as compared to the case of unfilled samples is obviously due to Umklapp-scattering processes induced more effectively by the low-energy phonon modes rather than energy dissipation by localized rattling modes of the guests [23,24].

Acknowledgement

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