Experimental report

17/03/2021

Proposal: 7-01-465 **Council:** 4/2017

Title: Effect of the dimensionality on the lattice dynamics and anharmonicity of thermoelectric silicides

Research area: Materials

This proposal is a new proposal

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Samples: CoSi
CrSi2

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	0	6	19/03/2018	26/03/2018
IN6	7	0		
IN4	3	2	21/03/2018	23/03/2018

Abstract:

We propose to investigate the lattice dynamics and the anharmonicity of CrSi2 and CoSi bulk and nanostructured alloys, and to understand the effect of the dimensionality on the phonon density of state and on the phonon scattering. Recently, previous studies on nanostructured Si and other thermoelectric materials have shown a strong increase of low energy vibrational modes through nanostructuration which should have large impact on thermal conductivity and it will be interesting to investigate other silicide compounds with large Debye temperature to confirm the universality of this behavior and better understand it. So far, despite its quite interesting properties for thermoelectric applications, CrSi2 has never been studied by inelastic neutron scattering and CoSi only under its bulk form. The results will be compared with ab-initio lattice dynamic calculation. The study of the temperature dependence will permit to determine how strong is the anharmonicity and to compare it with the effect of the nanostructuration.

Report of the experiment 7-01-465

During the 15 last years, new thermoelectric materials were found to be more efficient for high temperature thermoelectric generation following some simple concept such as the effect of the dimensionality on the thermoelectric properties of abundant and non toxic silicides alloys [1,2]. As for example, the nanostructuration can strongly decrease the thermal conductivity of silicides making them competitive with conventional thermoelectric materials in the temperature range 300 - 900°C.

Among silicides, promising candidates such as $CrSi_2$ and CoSi, after manganese and magnesium silicides, alloys have a Figure of Merit ZT about 0.25-0.3 (bulk materials) [2]. Their power factor $\alpha^2\sigma$ is similar to the best thermoelectric materials but their performances are limited by their high thermal conductivity (about 15 W/mK). Thermal conductivity measurements have been performed on densified nanocrystallites with about 50 to 70 nm grain size of both alloys and a strong decrease of the thermal conductivity by about 30 to 50 % has been observed [3-5].

The objective of this experiment was to investigate the lattice dynamics and the anharmonicity of both $CrSi_2$ alloys and CoSi alloys, bulk and nanostructured, and to understand the effect of the dimensionality on the phonon density of state and on the phonon scattering.

$CrSi_2$ alloys and CoSi alloys have been prepared by arc furnace followed by mechanical milling. By varying the mechanical milling conditions it is possible to obtain grains of different scale [3,5]. For both alloys, we will investigate the size effect on the phonon scattering. Three crystallites size have been chosen: >500nm in order to approach the bulk properties, ~60-70 nm and ~10-20 nm. Even if the samples are pretty stable in air, all the synthesis steps have been performed under inert atmosphere in order to avoid native oxidation and have been sealed under Argon for transportation to ILL. The INS experiments have been performed on both IN4 and IN6 and we have calculated the generalized density of states (GDOS) g(E) from the INS spectra using the incoherent approximation.

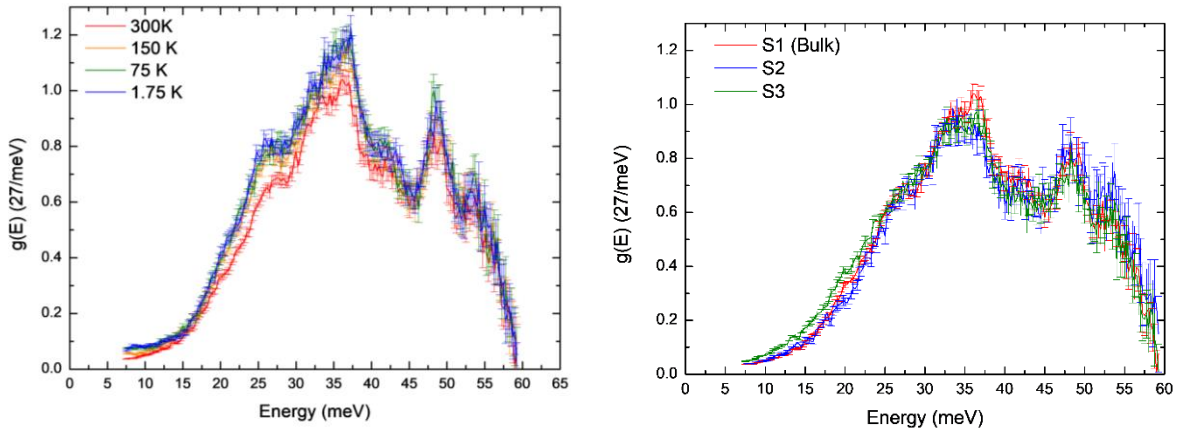

Figure 1 : (Left) Experimental GDOS of $CrSi_2$ sample S1 (Bulk) upon temperature variation measured with the TOF spectrometer IN4 for λ = 1.1 Å. (Right) Experimental GDOS of $CrSi_2$ samples S1 (Bulk), S2 (64 nm) and S3 (14 nm) measured with the TOF spectrometer IN4 for λ = 1.1 Å.

We show in the Figure 1 the GDOS of bulk $CrSi_2$ in function of temperature and the GDOS of the bulk sample compared to the nanostructured samples at 300 K. Throughout the temperature range 1.5 to 300 K the overall GDOS is not altered considerably. We observe however a moderate sharpening of distinct peaks and an upshift of peaks in the high energy range >35 meV upon cooling. The weak temperature effect on the phonon properties marks the S1 sample as a moderately quasi-harmonic crystal. A comparison of the GDOS of the bulk sample with our published DFT calculations [6] shows that the main features of the phonon DOS are observed in our experiments. Concerning bulk CoSi, the effect of temperature is weak and our results are very close to a prior study in the littérature [7].

In the nanostructured $CrSi_2$ samples, one observes a slight optical mode broadening and a downshift of ~1 meV (see Figure 1). Similar effect is observed in nanostructured CoSi.

For the sample S3 with the smallest grain size, there is an increase DOS below 25 meV. This strong increase of the low energy vibrational modes through nanostructuration could be due to a smaller Debye temperature induced by smaller grain size and/or defects, as in nanostructured Si [8,9].

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