Experimental report

12/11/2024

Proposal: 7-01-578 **Council:** 10/2022

Title: Inelastic neutron scattering studyof the lattice dynamics and anharmonicity of thermoelectric cubic SrSi2

Research area: Materials

This proposal is a new proposal

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Samples: NaGe
SrSi2

Instrument	Requested days	Allocated days	From	To
PANTHER	2	2	25/05/2023	27/05/2023
IN5	3	0		

Abstract:

We wish to study the lattice dynamics and phonon anharmonicity of cubic SrSi2 by inelastic neutron scattering. Cubic SrSi2 has been predicted to be a topological Weyl semimetal and to have quadratic double-Weyl phonons and is an excellent thermoelectric material with ZT up to 0.4 at 300 K. This is notably because it has a low thermal conductivity for a silicide compound. Our calculations indicate the presence of a low-energy optical mode with a rather high Grüneisen parameter which can be probed only with neutron spectroscopy because it is optically silent. As it will give a significant peak in the phonon DOS, inelastic neutron scattering experiments using a time of flight spectrometer will be a good choice in order to probe its anharmonicity and to understand its connection with the low thermal conductivity of cubic SrSi2. We, therefore, ask for temperature-and pressure-dependent inelastic experiments to study the vibrational properties responsible for thermal transport in cubic SrSi2 in every detail.

Scientific background

Thermoelectric materials (TEM) attract high interest from many fields of science as a potential green energy resource. The major field of application of TEMs is the conversion of waste heat to electric energy via the Seebeck effect [1]. For a few decades the TEM community has been on the quest for more efficient and environment friendly compounds. The TEM efficiency is represented by the dimensionless figure of Merit ZT = $\frac{\sigma S^2}{k}$, where S is the Seebeck coefficient, σ is the electrical conductivity, and k is the thermal conductivity. The power factor (PF) $S^2\sigma$ can be optimized by tuning the charge carrier concentration into the range of semiconducting materials. Hence, a further improvement of ZT requires semi-conducting materials of poor thermal conductivity. At present, the drawback of the best-performing TEM compounds is their toxicity, rareness, and/or costs of the chemical elements they are synthesized from. For this reason, silicides have attracted high interest because they are made of abundant, cheap, and non-toxic elements.

Among silicides, cubic $SrSi_2$ has attracted the attention because of its good thermoelectric properties at the vicinity of the room temperature. A ZT of 0.15 was obtained for undoped $SrSi_2$ at 300 K [2] and ZT as large as 0.4 was reached for yttrium-doped $SrSi_2$ at 300 K [3] thanks to its moderate thermal conductivity (κ = 4-5 W/m.K) [2-3] compared to most of the silicides [4] and despite its simple cubic crystal structure containing 12 atoms. This suggests higher anharmonicity in $SrSi_2$ than in other silicides. Recent theoretical works suggested that cubic $SrSi_2$ could be a topological Weyl semimetal [5] and the presence of quadratic double-Weyl phonons [6], making this material very attractive for topological science. However, despite the interest of this material, until now there is no experimental study of the lattice dynamics and the DFT study in ref. 6 was limited to the phonon dispersion curves of $SrSi_2$.

Experimental details

We have performed Inelastic Neutron Scattering (INS) experiments on single-phase powders of cubic $SrSi_2$. With the time of flight (TOF) Panther spectrometer. The experiments have been performed at 2 K, 100 K, 200 K and 300 K with the incident energies Ei = 76 and 19 meV to monitor the Stokes line for the complete Phonon Density of States (PDOS) and for the low-energy Sr-dominated phonon excitations, respectively. We have also calculated the neutron weighted DOS for analyzing the experimental data.

Experimental results

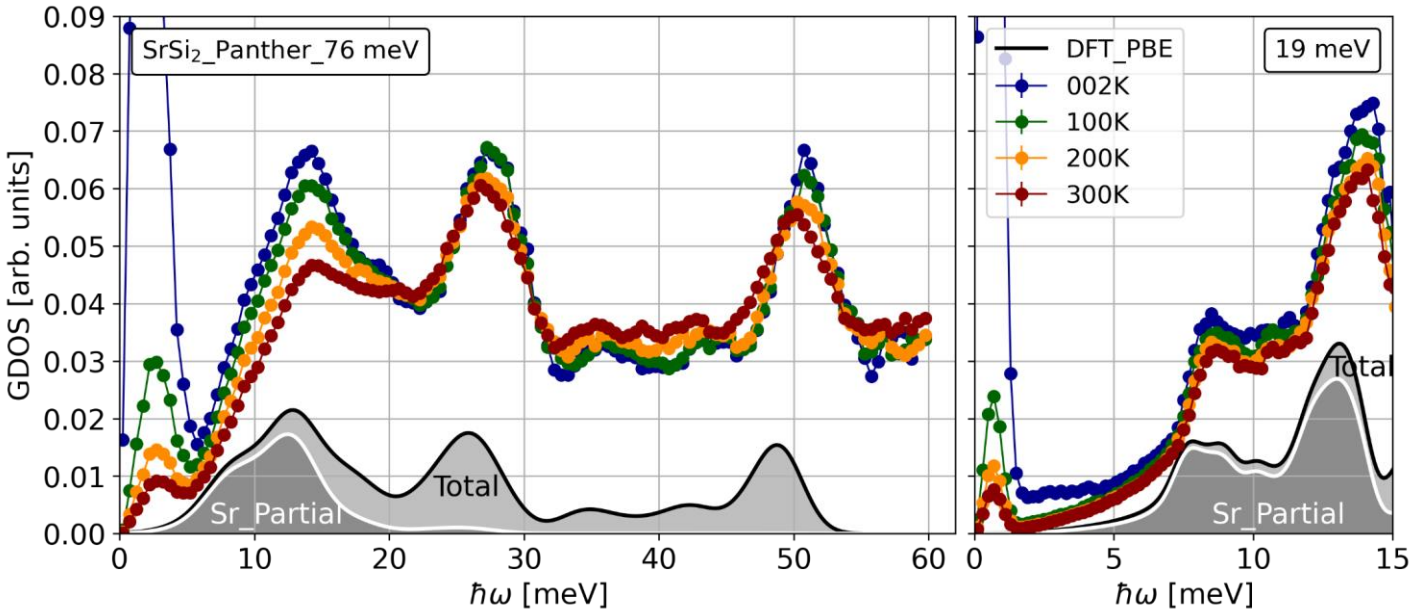

Figure 1 : GDOS of $SrSi_2$ derived from data measured at the indicated temperatures with Panther with 76 meV (left) and 19 meV (right) incident energies.. Total and Sr partial DOS derived from DFT lattice dynamics calculations are reported with the experimental data.

In the Figure 1, we report the Generalized DOS (GDOS) obtained from the INS spectra at 2 K, 100 K, 200 K and 300 K for both 76 meV and 19 meV incident energies. We compare the GDOS with DOS results calculated using DFT with PBE functional approximation and convoluted with aGaussian functions for resolution effects. The elastic peak is noticeable within the range of 1-5 meV, and its intensity diminishes as the temperature rises. In the case of the experiment with 76 meV incident energy, at $\hbar\omega$ >10 meV, we observe three distinct inelastic peaks at approximately 15, 27, and 50 meV. They corresponds well with the DFT calculations and correspond to several localized-optical modes involving mainly Sr motions and Si motions for the lowest energy mine and the two higher energy lines, respectively. The experiment with 19 meV incident energy on the right side of Figure 1 permit us to discern a breakdown of the initial strong peak observed at 15 meV in the low-resolution data on the left side of Figure 1 into three distinct peaks positioned around 8.6 and 10.6 and 14 meV. According to our DFT calculations, the peak at about 8.6 meV corresponds to both acoustical phonons at the Brillouin zone boundaries and to the lowest energy optical mode. This higher resolution also exposes more subtle well-defined features located between these two peaks. Obviously, the different resolutions convoluted with DOS calculated from the DFT lattice dynamics reproduce the GDOS data. Notably, all the predicted peaks are present with a slight energy shift of the DOS toward lower energy with respect to the GDOS. This is due to the larger volume obtained in the DFT calculations which leads to weaker bonding and thus to smaller force constants and phonon energies.
In the figure 1, one can see clearly the temperature dependence of the characteristic phonon energies. They downshift with increasing temperature. To quantify these energies, we conducted fits for the GDOS using Gaussian functions. We found that the peak at 8.4 meV has no significant change in energy with temperature whereas the energy of the other phonon peaks exhibited a decrease of approximately 1.5 % as the temperature increased from around 2 to 300K. The absence of temperature dependence of the line at 8.4 meV is surprising because our DFT calculations have predicted rather large Grüneisen parameter for the optical mode at this energy. This call for further experiments under high pressure for determining the experimental value of the Grüneisen parameters of the different features observed in the present INS experiments.

Note that the study is part of the Ph. D thesis of Doaa Omar Abdelaziz ALI within the Ph.D program of the ILL on the alkaline / alkaline-earth and group IVA alloys for energy applications and part of the Ph. D thesis of Rana Ghannam on the thermoelectric properties of $SrSi_2$.

References

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