CHEMISTRY: MOLECULES TO MATERIALS

Institut Charles Gerhardt Montpellier

Lattice dynamics study of thermoelectric cubic $SrSi_2$ by Raman scattering experiments and ab initio calculations

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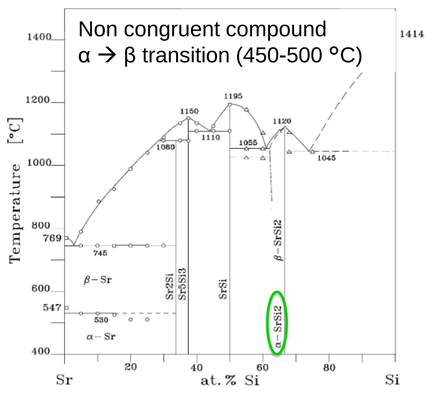
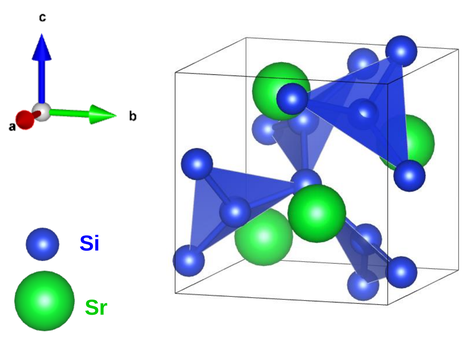
Introduction

Thermoelectric materials (TEM) attract high interest from many fields of science as a potential green energy resource. For a few decades the TEM community has been on the quest for more efficient and environment friendly compounds. 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. In the present work, we present a combined pressure dependent Raman scattering study and ab initio study of the lattice dynamics of cubic $SrSi_2$. We find 5 of the 8 Raman-active modes predicted by the theory, but one of the missing mode is overlapping another observed mode. Good agreement is found for the frequencies and the calculated Grüneisen parameters follow qualitatively the experimental trend. We notably show that the phonons in the intermediate range 150-300 cm^{-1} have low Grüneisen parameters (less than 1) whereas moderate Grüneisen parameters (above 1) were found above 300 cm^{-1}. However, we found that the low energy optical mode predicted at 7.5 meV, which is optically silent, has large Grüneisen parameter (about 2.5) and its interaction with the acoustical phonons could explain the rather low lattice thermal conductivity of $SrSi_2$ compared to most of the silicides.

Choice of Strontium silicide α-$SrSi_2$



Palenzona and al, JALCOM, 2004



α-$SrSi_2$
Cubic ($P4_332$)
a=b=b= 6.5450 Å

Abundance of Sr and Si
Eco-friendly

Thermoelectric properties of pure α-$SrSi_2$

S = 130 µV/K at RT
$S^2\sigma$ (α-$SrSi_2$) = 0.9 mW/mK²
ZT_{max}= 0.05 - 0.15

BUT λ= 5-6 W/m.K (pure)

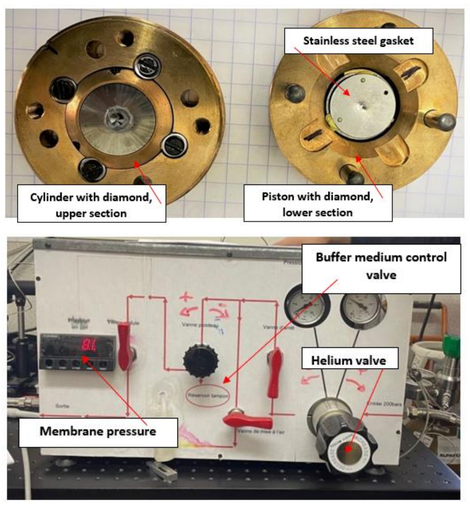
Lue et al., Appl. Phys. Lett. , 2009
Singh et al, Intermetallics, 2020

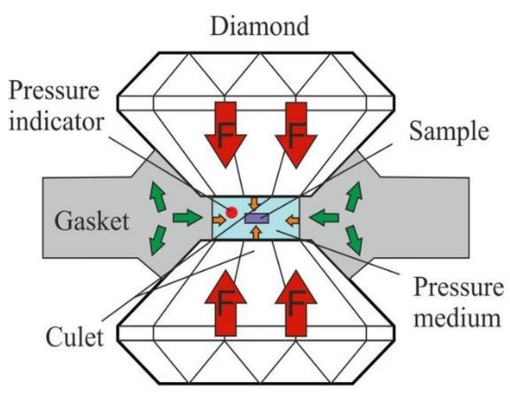
Objectives and strategies

The aim of this work is to study the anharmonicity by determining the Gruneisen parameters of the active modes in Raman using combined pressure dependent Raman scattering study and ab initio study of the lattice dynamics of cubic $SrSi_2$.

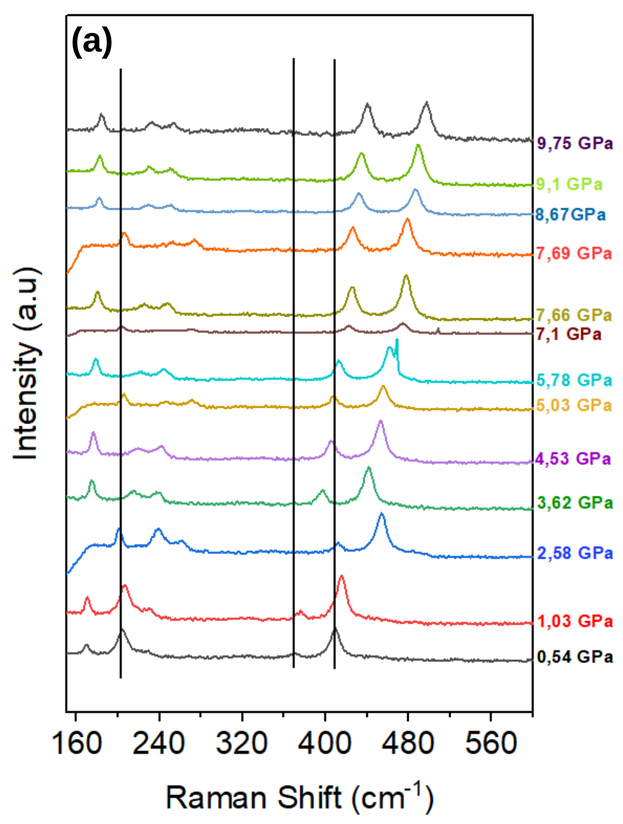
Results and Discussion

❖ Experimental work (0.54- 9.75 GPa)

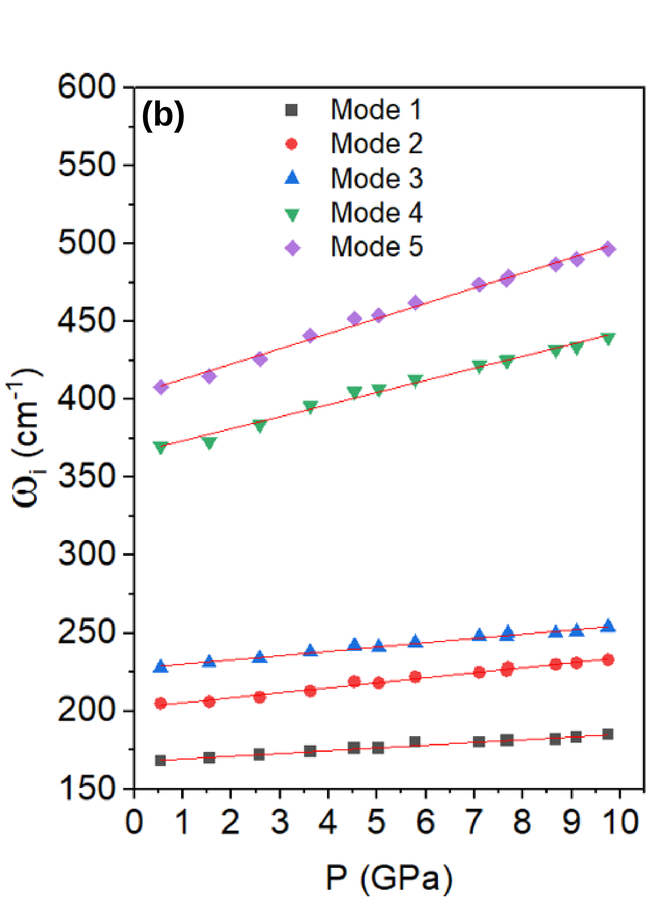




- High pressures was achieved using diamond anvil cell (DAC)
- Pressure was monitored using Ruby Fluorescence
- The uniaxial pressure supplied by the (DAC) was transformed into uniform hydrostatic pressure using a pressure-transmitting medium (Methanol-Ethanol)



(a) Raman spectra on bulk polycrystalline α-$SrSi_2$ (2N-bulk) between 0.54 GPa and 9.75 GPa



(b) Evolution of the frequencies of the Raman-active vibrational modes with pressure.

❖ Between Calculs and Experiment

The primitive lattice of α-$SrSi_2$ contains 12 atoms and therefore has 33 optical modes and three acoustic modes responsible for the decrease in thermal conductivity. Group theory predicts the following decomposition into irreducible representations for the vibrational modes at the centre of the Brillouin zone:

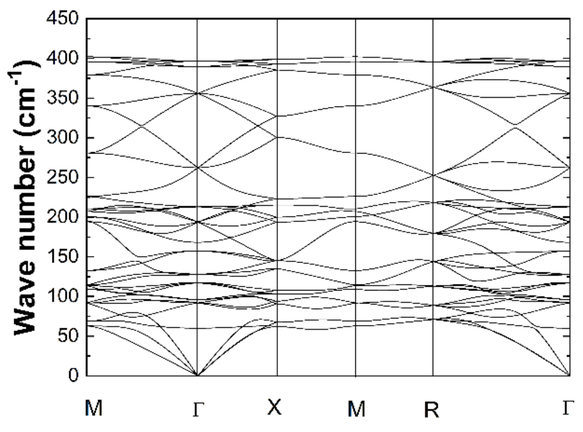
$$\Gamma = 1A_1 \oplus 2A_2 \oplus 3E \oplus 4T_2 \oplus 5T_1$$

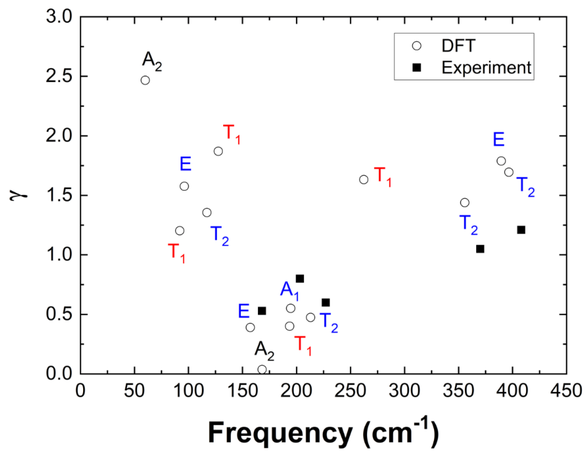
Modes	Symmetry	Frequencies at RT (DFT)	Frequencies at RT (Exp)	$d\omega_i$ /dP (cm^{-1}/GPa)	Paramètre de Grüneisen γ_i^T
Mode 1	E (1)	157.3	168	1.76	0.53
Mode 2	A_1	194.6	203	3.21	0.80
Mode 3	T_2 (2)	213	227	2.74	0.60
Mode 4	T_2 (3)	355.8	370	7.75	1.05
Mode 5	T_2 (4) + E (3)	389.5	408	9.74	1.21

$$\gamma_i^T = -\left(\frac{\partial ln(\omega_i(P,T))}{\partial \ln(V(P,T))}\right)_T = B\left(\frac{\partial \ln(\omega_i)}{\partial P}\right) = B\frac{1}{\omega_i}\frac{\partial \omega_i}{\partial P}$$

γ_i^T: Grüneisen parameter of a vibrational mode active in Raman at RT
ω_i : Vibrational frequency of a mode i
P: Pressure
B: the Bulk Modulus of α-$SrSi_2$ determined experimentally by DRX under pressure and of value B = 50.3 GPa

Grüneisen parameter γ_i^T significantly less than 1 for vibration modes with frequencies below 300 cm^{-1} and greater than 1 for vibration modes with frequencies above 300 cm^{-1} which essentially involve displacements of Si atoms.





Rather good agreement between DFT calculations and Raman experiments.
The low energy mode with A_2 symmetry has large Grüneisen parameter γ_i^T= 2.5 → very anharmonic mode that could strongly interact with acoustic phonons.

Perspectives

Raman experiments as function of temperature will better probe the anharmonicity, notably through the temperature dependence of linewidth → under way
Inelastic neutron scattering and infrared experiments for probing A_2 and T_1 modes → under way

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