

## Stability and thermodynamic properties of phases in the Li-Si system

The calculation of thermodynamic properties for the known crystalline phases using first principles methods based on density functional theory (DFT) has been our focus. In particular we developed the tools to calculate the free energy without any free parameter or experimental input. This allows to estimate other thermodynamic data like specific heat which can then directly compared with the experimental data obtained by the Mertens group.

Standard DFT calculations normally correspond to zero temperature, however using the quasi-harmonic approximation to calculate the phonon dispersion for different volumes, one can reintroduce temperature via the vibronic contributions to the entropy. This approximation allows to obtain the free energy  $F(V, T) = U(V) + F_{vib}[\omega(V), T] + F_{el}(V, T)$ , with  $U$  being the internal energy calculated via DFT,  $F_{vib}[\omega(V), T]$  the contribution of the lattice vibrations, and  $F_{el}(V, T)$  the electronic excitations.

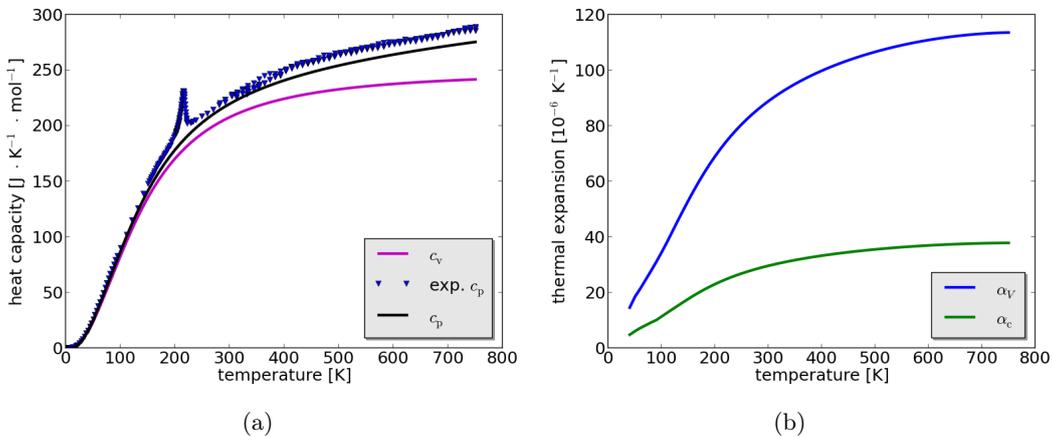


Figure 1: Calculated heat capacity compared to experimental values from the Mertens groups (a) and thermal expansion coefficient (b) for the Li<sub>7</sub>Si<sub>3</sub> phase.

The main interest of the research project has been the accurate determination of thermodynamic data for the lithium-silicide system. Therefore, we calculated for Li<sub>7</sub>Si<sub>3</sub> and Li<sub>15</sub>Si<sub>4</sub> the heat capacities under isotropic volume expansion. In case of LiSi, which contains a smaller number of atoms compared with the other phases we are even able to obtain the anisotropic thermal expansion coefficients. The agreement with the experimental  $C_p$  values is very good as shown in Fig 1a. The thermal expansion displayed in Fig. 1b has not been measured so far and can be considered as theoretical prediction.

## Search for stable phases in the Li-Si system

The evolutionary algorithm for crystal structure prediction developed at our institute [1] has been used at the moment only to verify existing structures with known stoichiometric ratios. The known structures Li<sub>7</sub>Si<sub>3</sub> and Li<sub>13</sub>Si<sub>4</sub> have been reproduced. An additional structure for Li<sub>13</sub>Si<sub>4</sub> has been found, too. For LiSi and Li<sub>15</sub>Si<sub>4</sub> only parts of the crystal structure, which can be seen as building blocks of the unit cell, have been found. This fact indicates that there is no deep energy minimum which could be a hint for a tendency to create defects and the difficulties to synthesize single crystals. As the system size gets bigger, the combinatorial possibilities increase exponentially. Due to the size of the unit cell

(about 100 atoms), we have not investigated the  $\text{Li}_{12}\text{Si}_7$  and  $\text{Li}_{21}\text{Si}_5$  phases in a systematic way.

## Diffusion properties

We carried out first principles DFT molecular dynamics simulations for perfect crystalline phases in the Li-Si system to obtain the Li self-diffusion coefficients. The calculation of the mean square displacement allows to determine diffusion coefficients using the Einstein relation. We carried out constant NVT simulations for  $\text{LiSi}$ ,  $\text{Li}_7\text{Si}_3$ ,  $\text{Li}_{13}\text{Si}_4$ ,  $\text{Li}_{15}\text{Si}_4$ , and  $\text{Li}_{21}\text{Si}_5$ . At low temperatures (below 600K) the atoms move around their equilibrium positions. In case of  $\text{LiSi}$  we obtain the same ratio of about 2 for the Li/Si diffusion coefficient as found in [2]. Comparing different phases, the  $\text{Li}_{15}\text{Si}_4$  phase shows the highest diffusion coefficient, about 2 orders of magnitude higher than the value for  $\text{LiSi}$ . As a general trend one finds that with increasing Li content of the phases the diffusion coefficient for Li atoms increases faster than the ones of Si atoms. In case of the  $\text{Li}_{21}\text{Si}_5$  the ratio increases, indicating a much higher mobility for Li atoms. At higher temperatures atoms start to leave the lattice sites. While Li atoms show on average a higher diffusion coefficient compared with the Si atoms, both atoms start to move around which results in a weakening of the bonded Si networks destroying the crystal structure. This observation is in agreement with the finding in [2] and with the results from [3] on amorphous structures.

## Li mobility/transport in crystalline phases

Lithium silicides can be used as electrode materials and therefore the lithium diffusion process is a crucial property. Our previous first principles DFT molecular dynamics calculations on the Li self-diffusion have been carried out for perfect crystalline systems only. The  $\text{Li}_7\text{Si}_3$  phase has been characterized by crystallography with 2/3 occupation of Li on some lattice sites. We account for this fact in the simulation by using larger cells with vacancies. Our previous first principles molecular dynamics simulations find significantly enhanced mobility of the Li atoms close to the vacancies at temperatures where the other atoms still remain at their position. In the next funding period we plan to include the effect of Li vacancies in the crystal on the diffusion properties. This allows us also to go away from the well-defined Li content of the pure phases. The molecular dynamic simulations at various temperatures should also deliver information on the stability of phases during the lithiation/delithiation process. Using the elastic nudged band method we will also calculate energy barriers for diffusion along certain pathways. The goal of this working package is to obtain information on diffusion pathways and diffusion coefficients which are of interest in order to understand the lithiation/delithiation process.

## References

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- [2] H. Kim, C.-Y. Chou, J. G. Ekerdt, G. S. Hwang, *J. Phys. Chem. C* **2011**, *115*, 2514–2521.
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