Department of Materials Research by Computers

DFT study of the structural phase transition in $LiFeSi_2O_6$

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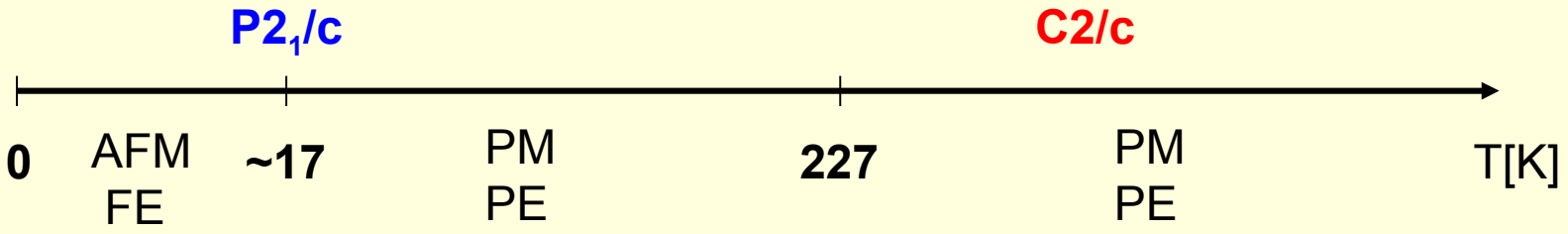
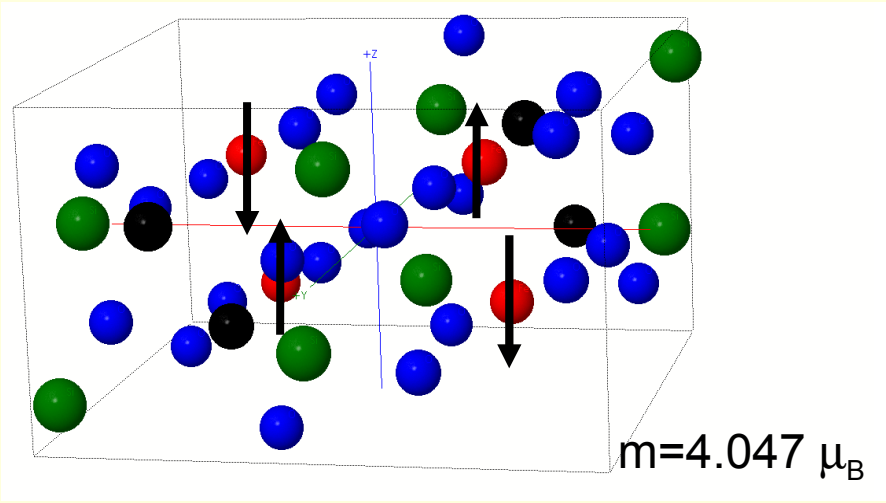
Li-aegirine

- Belongs to the pyroxenes - a group of important rock-forming silicate minerals found in many igneous and metamorphic rocks.
- Crystallize in the monoclinic structure
- Has two phases – high temperature C2/c phase and low temperature $P2_1/c$ phase. $P2_1/c \subset C2/c$
- It is an antiferromagnetic with $T_N = 17.5$ K
- It is a multiferroic - coexistence of magnetic and ferroelectric order



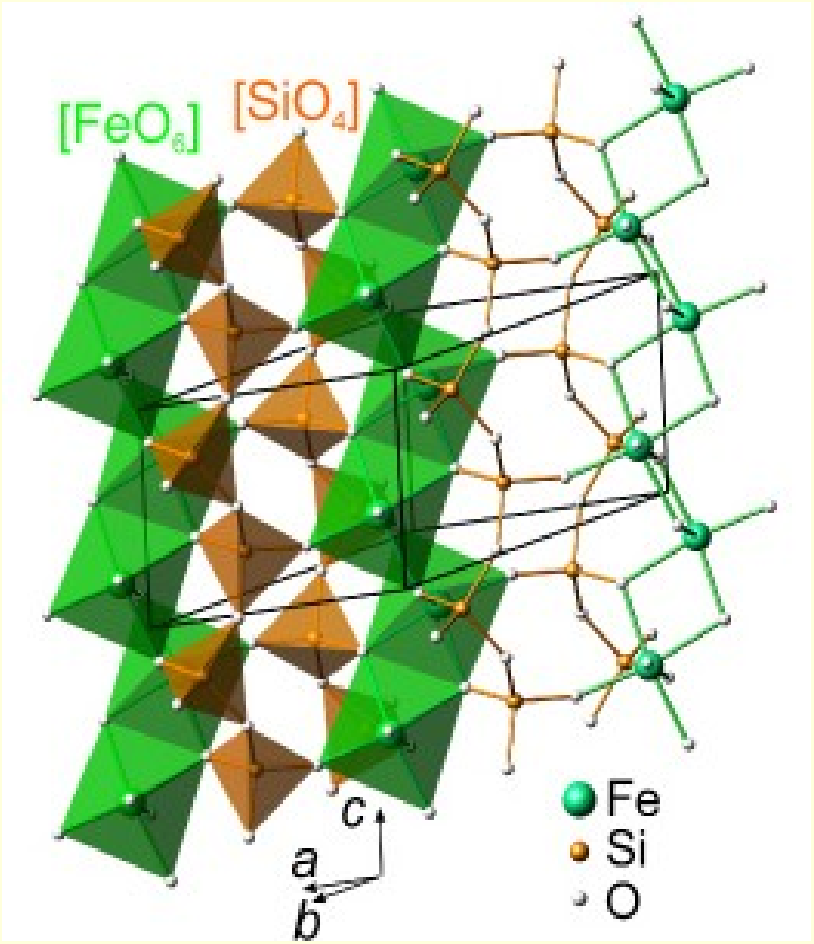
Calculation details

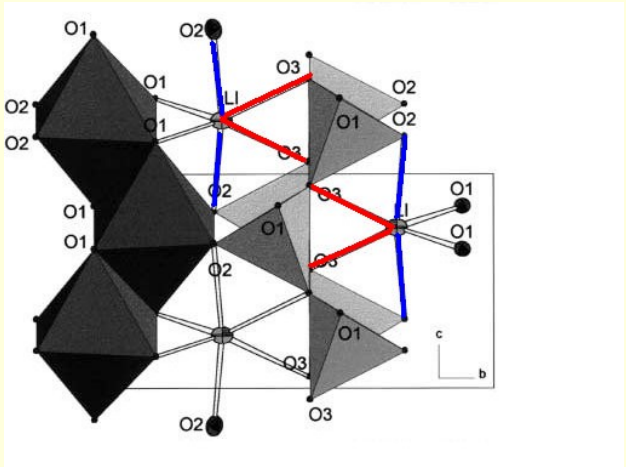
- For calculations (DFT) of crystal structure the VASP package was used with PAW/PBE atomic data and Generalized Gradient Aproximation (GGA)
- Phonons were calculated using PHONON software
- Calculated supercells contained 40 atoms for C2/c structure, and 80 atoms for $P2_1/c$ structure
- All calculations have been performed with the AF magnetic order



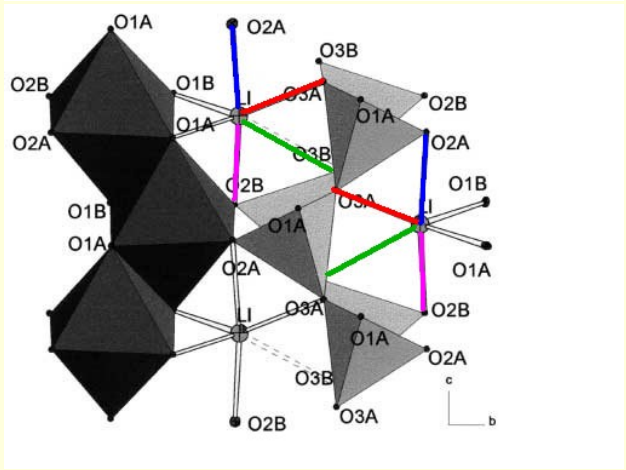
Crystal structure

The general formula of pyroxenes is **AMSi$_2$O$_6$**, where
A stands for alkali metal such as Li, Na, K, etc.
M stands for metal ions such as Fe, Mn, Cr, Al, etc





C2/c
T>227 K



P2$_1$/c
T<227 K

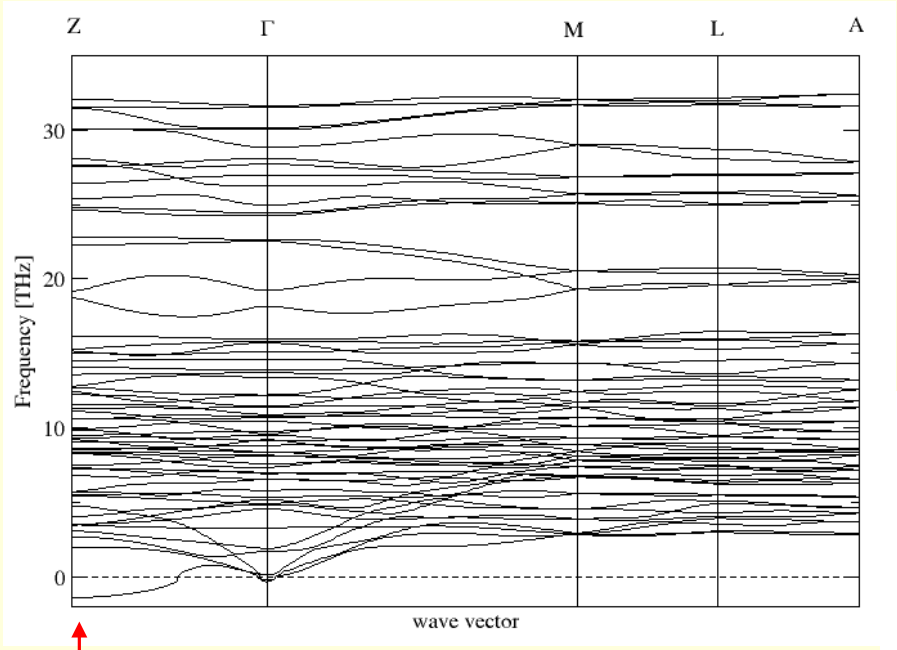
Comparison of experimental and calculated lattice parameters

	C2/c		$P2_1/c$	
	Exp (T=298K)	Calc	Exp (T=100K)	Calc
a [Å]	9.66	9.86	9.62	9.83
b [Å]	8.66	8.89	8.66	8.88
c [Å]	5.29	5.36	5.26	5.33
β	110.19	111.02	109.95	110.8

$P2_1/c$ – G.J.Redhammer et al, Phys and Chem of Minerals 28 (2001) 337-346
C2/c – G.J.Redhammer et al, Zeitschrift fur Kristallographie 219 (2004) 278-294

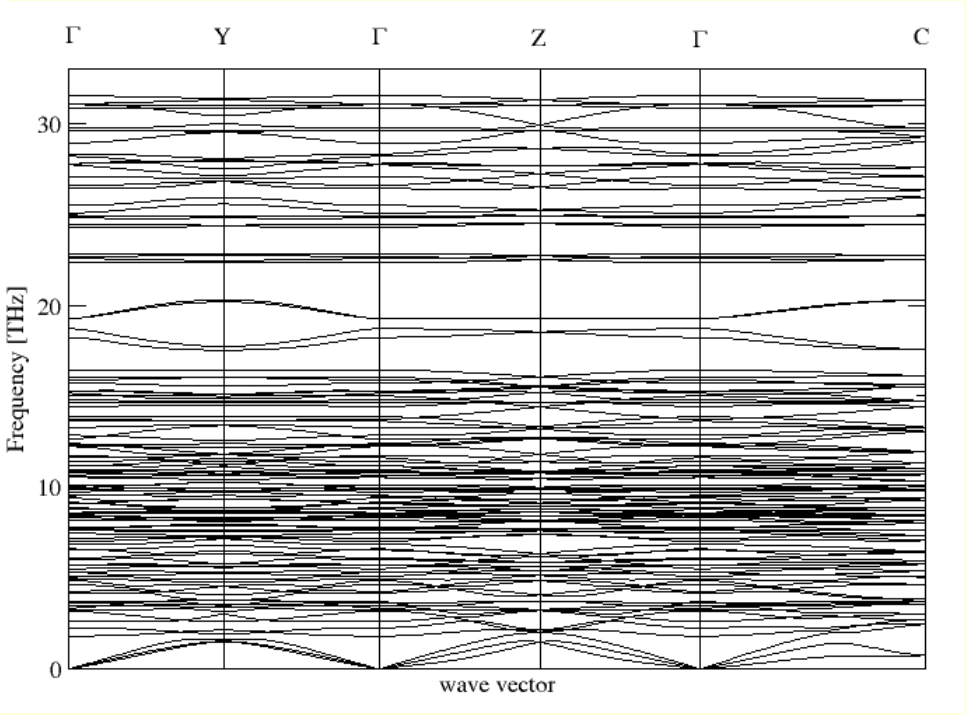
Phonons

Phonon dispersion curves in p = 0 GPa



C2/c
60 branches

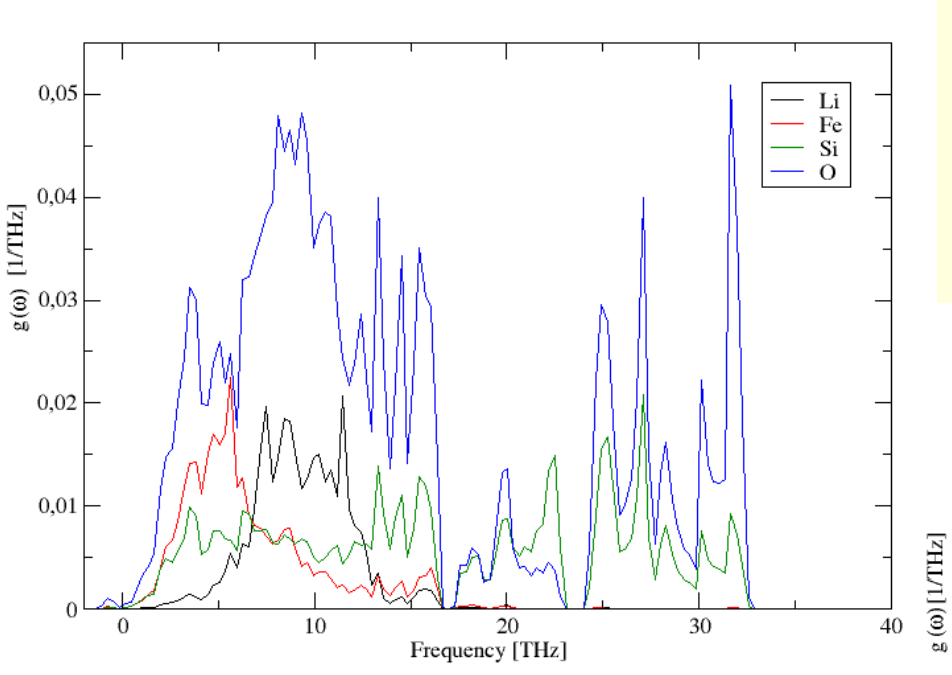
$P2_1/c$
120 branches

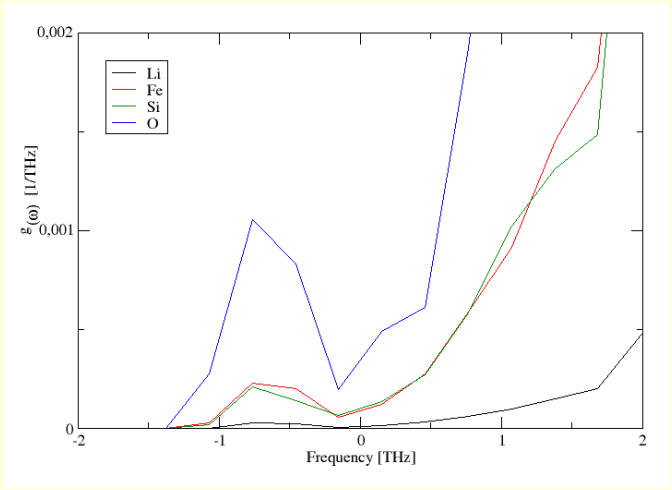


Soft mode which is responsible for phase transition from C2/c to $P2_1/c$

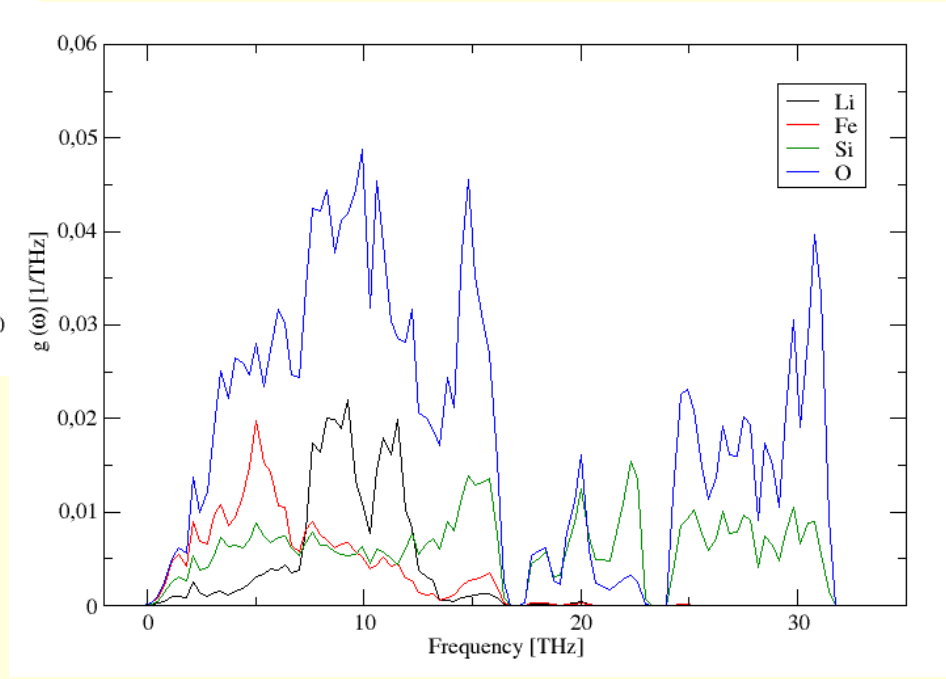
Phonon Density Of States (pDOS)

C2/c



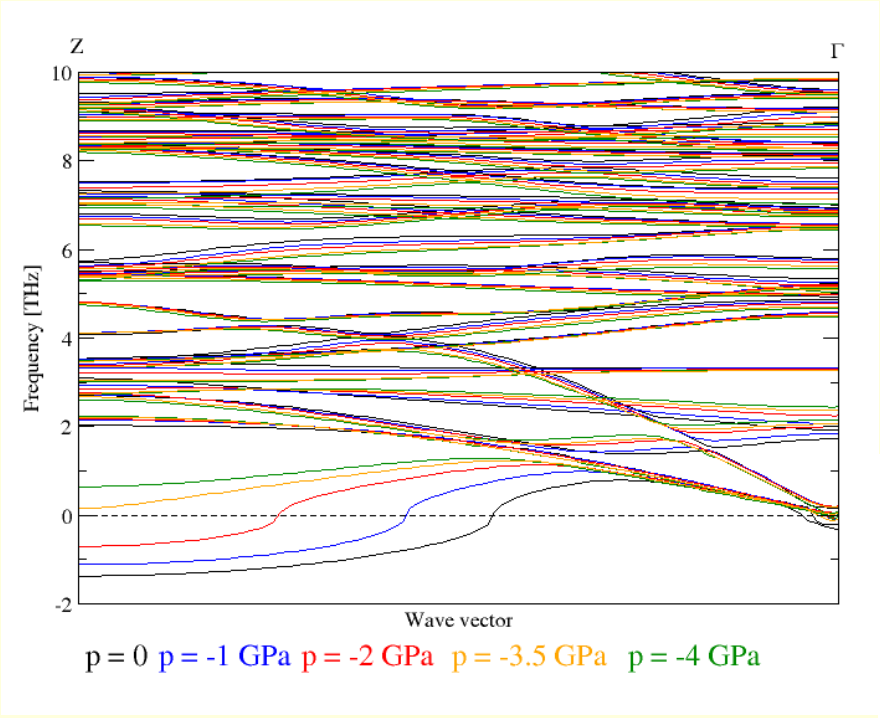


$P2_1/c$

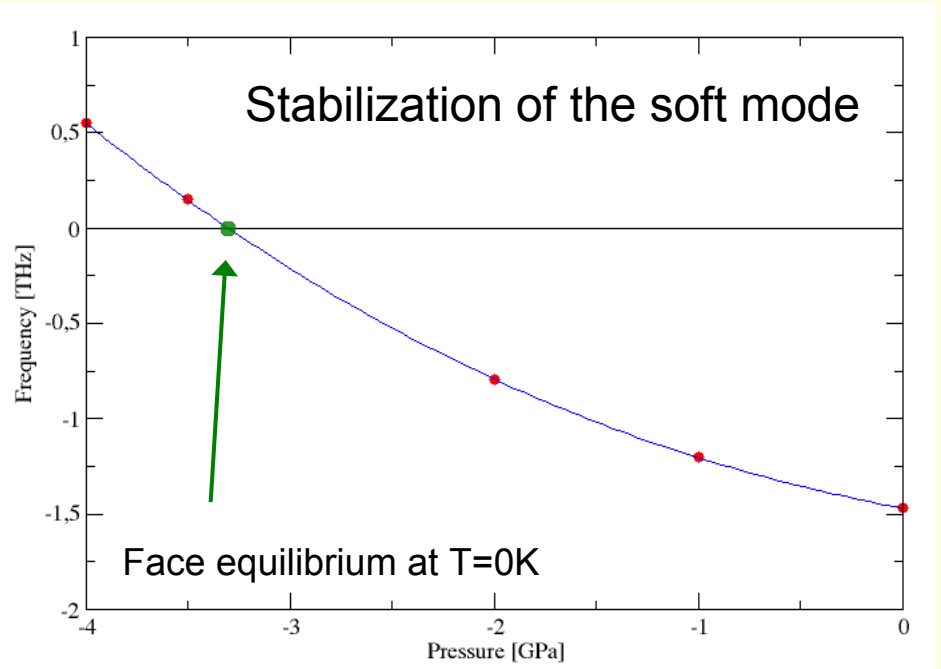


Pressure-dependence of the soft mode

Phonon dispersion curves for p ≠ 0 GPa

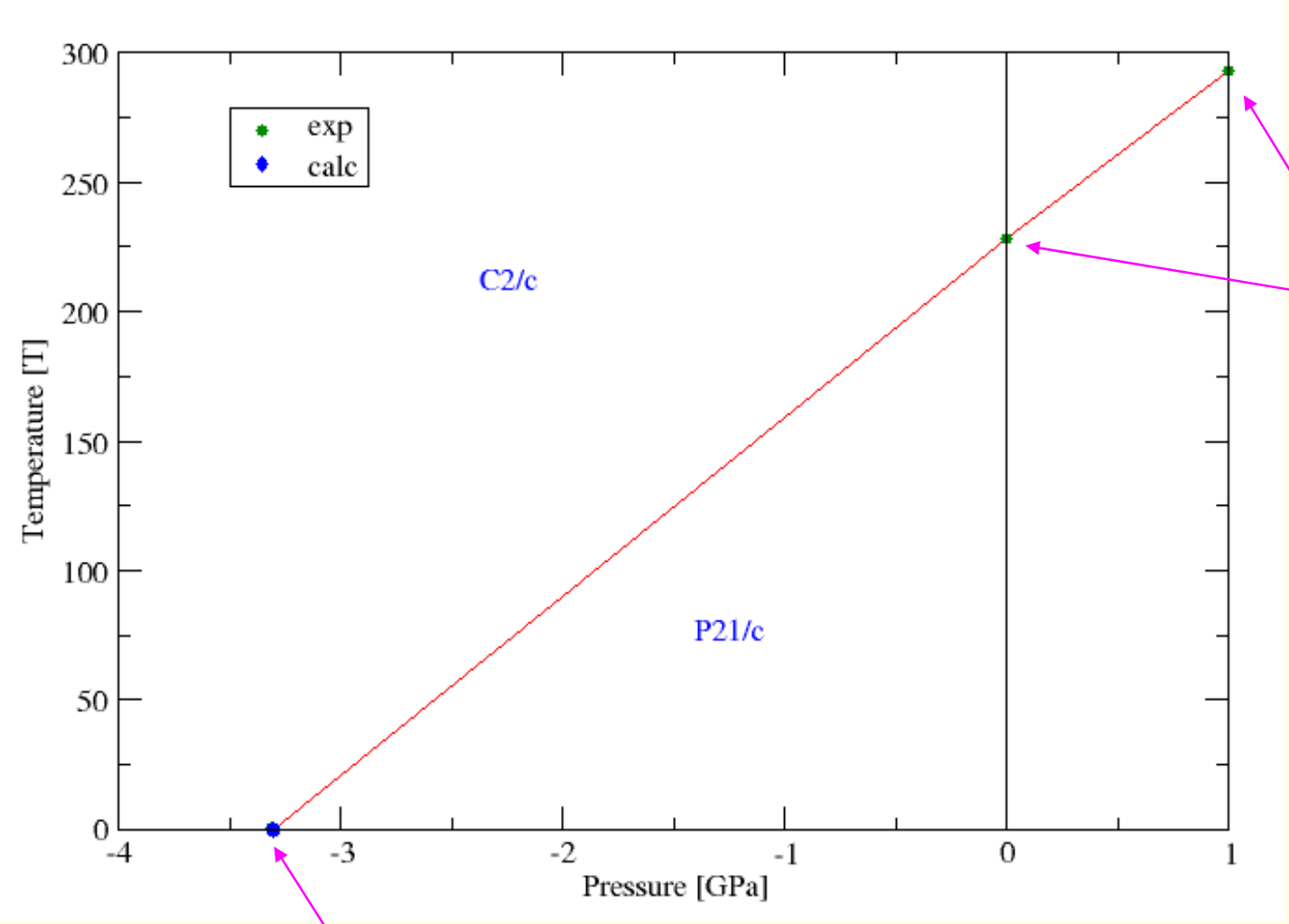


Calculations were performed only for the C2/c phase of $LiFeSi_2O_6$



The pressure of the C2/c → $P2_1/c$ phase transition for temperature of 0 K is p= -3.306 GPa

Phase diagram of Li-aegirine



Experimental points

My calculated point (-3.306, 0)

Conclusions

- We did calculations for two phases of LiFeSi2O6: high temperature phase C2/c and low temperature phase P21/c
- Calculated lattice parameters are in a good agreement with experimental data
- Phonon dispersion curves and phonon densities of states have been calculated for both phases of Li-aegirine for the first time
- We discovered soft mode responsible for the phase transition C2/c $\longrightarrow$ $P2_1/c$
- The calculated point of phase equilibrium at T=0 K is consistent with the experimentally constrained boundary

THANK YOU

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