# MS31-P4 Stabilization of dynamically unstable cystal structures in the Decoupled Anharmonic Mode Approximation (DAMA)

Donat J. Adams[1]

1. Reliability Science and Technology Laboratory Empa, Swiss Federal Laboratories for Materials Science and Technology Ueberlandstrasse 129 CH-8600 Dübendorf

email: donat77adams@gmail.com

The combination of experimental structure determination with *ab initio* simulations allows to refine structures with poor data. Still, this complementation is difficult, especially when it comes to crystal structures at high temperature or to temperature driven phase transitions: there the observed high temperature crystal structures often appear unstable once they are recalculated *ab initio*.

We therefore have developed a formalism (DAMA, [1,2]) that allows to calculate the vibrational free energy using DFT even for materials which exhibit negative curvature of the potential energy surface with respect to atomic displacements. Our novel solver allows to calculate the true vibrational states of the anharmonic potential in a non-perturbative way.

We apply the DAMA to the perovskite cryolite ($Na_3AlF_6$) and investigate the phase transition from the $P2_1/n$ to the *Immm* space group at a critical temperature between 710 and 950 K (experimental value 885 K [3]). We thus show that the free energy can stabilize crystal structures at finite temperatures which appear dynamically unstable at $T = 0$. Furthermore for cryolite we calculate the main axes of the thermal ellipsoid and can explain the experimentally observed increase of its volume for the fluorine by 250% at $T_C$.

Our calculations suggest the appearance of tunnelling states in the high temperature phase with a degenerate vibrational spectrum.

We compare our method to other approaches like the solution of effective Hamiltonians using Monte Carlo simulations or molecular dynamics, the SCAILD[4] and SSCHA [5]. We investigate the convergence of the vibrational DOS and of the critical temperature with respect of reciprocal space sampling using the polarizable-ion model.

From these very promising tests we conclude, the the DAMA formalism is computationally fast because it avoids statistical sampling and is completely *ab initio*. It is free of statistical uncertainties and independent of model parameters, but can give insight into the mechanism of temperature-driven structural phase transitions.

[1] Adams and Passerone, *submitted* (2016)

[2] Adams, Solid State Ionics, *in press* (2016)

[3] Yang et al. Phys. Chem. Minerals 19, 528 (1993)

[4] Souvatzis et al. Phys. Rev. Lett. 100, 095901 (2008)

[5] Errea et al. Phys. Rev. B 89, 064302 (2014)

[6] Zhong and Vanderbilt, Phys. Rev. B 53, 5047 (1996)

[7] Müller et al., Z. Physik B Cond. Matt. 84, 277 (1991)

[8] Bednorz and Müller, Z. Physik B Cond. Matt. 64, 189 (1986)

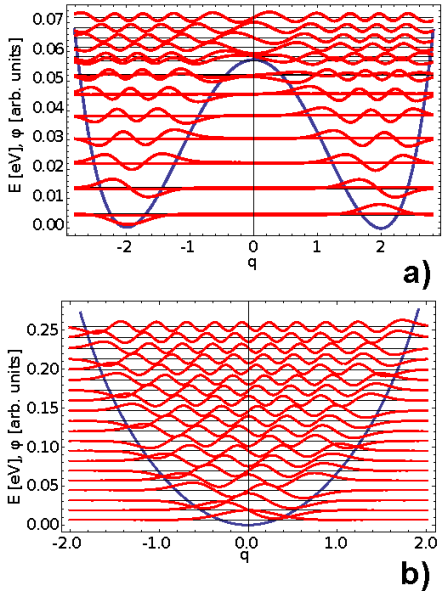


**Figure 1.** Eigenstates a) for the monoclinic and b) for the orthorhombic of cryolite, which due to delocalized ions in other crystals could give rise to physical properties such as multiferroicity [6], high dielectric constant [7] and superconductivity [8] .

**Keywords:** High temperature crystal structure, vibrational ellisoid, high temperature phase transition, ab initio calculations, free energy calculation, cryolite