Role of Surface Effects in the Vibrational Density of States and the Vibrational Entropy in Spin Crossover Nanomaterials: A Molecular Dynamics Investigation

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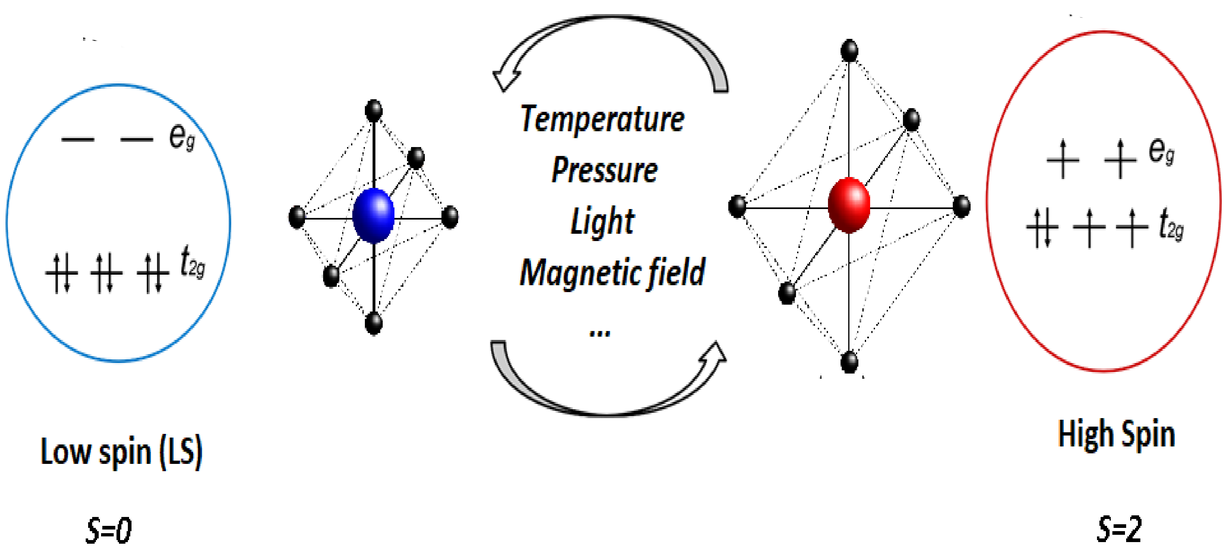
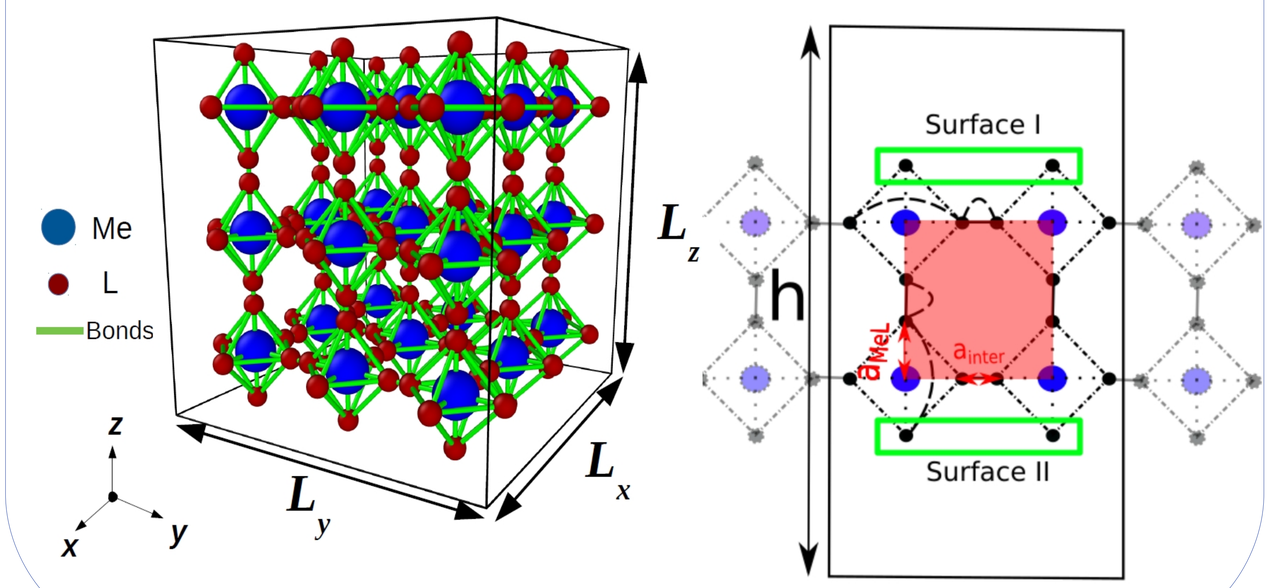
Introduction

In the last decade, spin crossover (SCO) nanomaterials have become attractive to many researchers and industries, as they are good candidates in the field of nanoelectronics, nanophotonics, nanosensors… However, size reduction effects can undesirably impact the switchable properties of SCO materials. In particular, phase stability properties are often modified and bistability phenomenon can be drastically altered when the size of these materials reaches the nanometer scale. Numerical Monte-Carlo simulations using spin-phonon and nanothermodynamics models successfully reproduce the phase stability deviation in SCO nanomaterials. Until now, however, vibrational properties of SCO coordination nanoobjects measured by nuclear inelastic scattering techniques (NIS) have been unsatisfactory modeled since surface effects have not been fully taken into account.
In our study, we aim to numerically investigate surface vibrational properties of nanoscale SCO thin films using molecular dynamics simulations. In particular, we focused on the influence of free surfaces on the size evolution of thermodynamic quantities such as the vibrational entropy [1,2,3].

Spin crossover materials



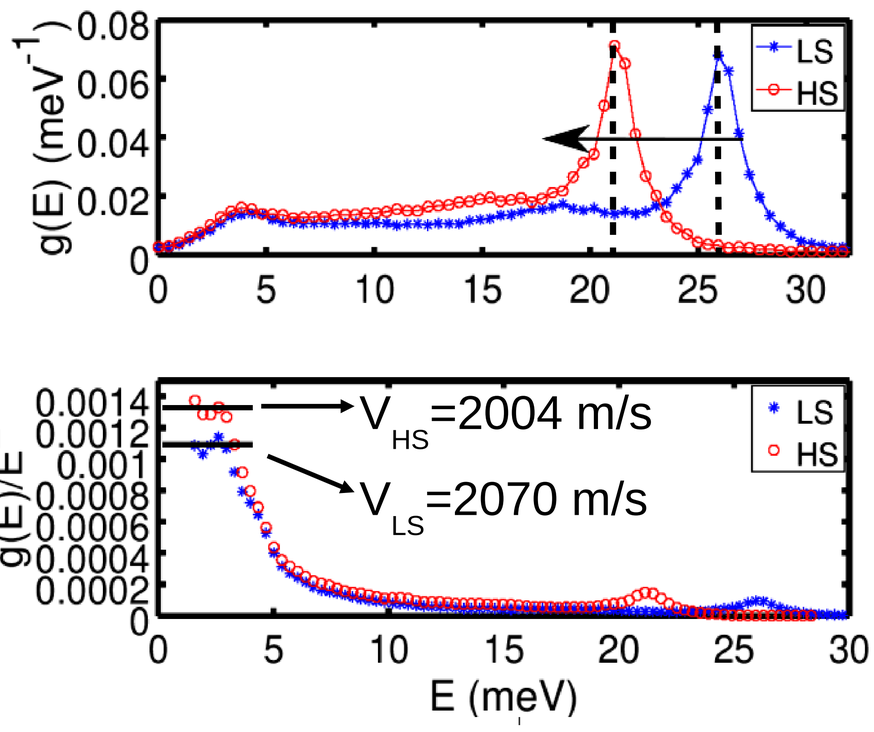
Material & method



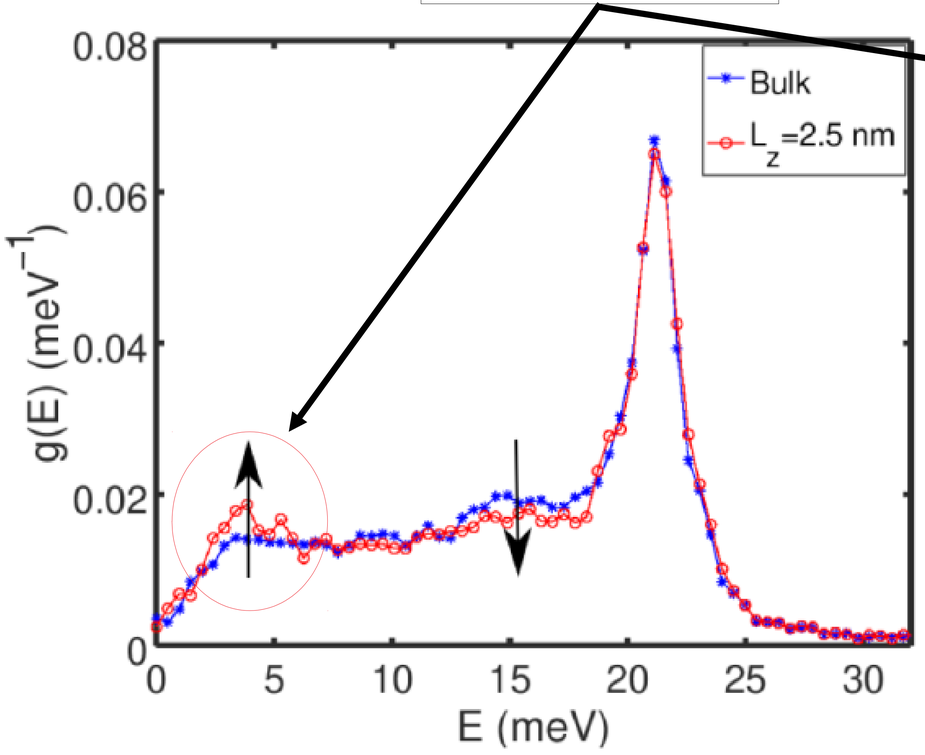
Results

Me-L optical modes (cm^{-1})

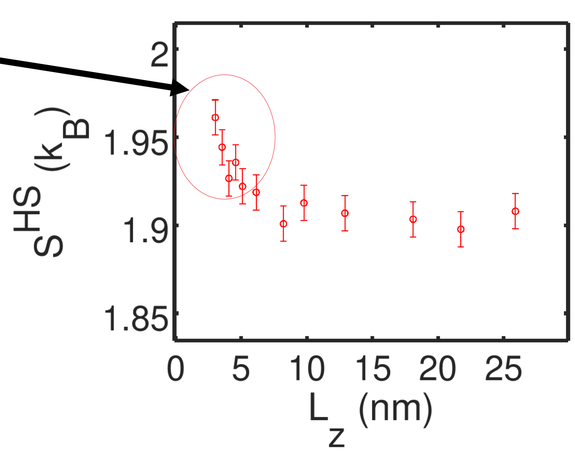
168 208



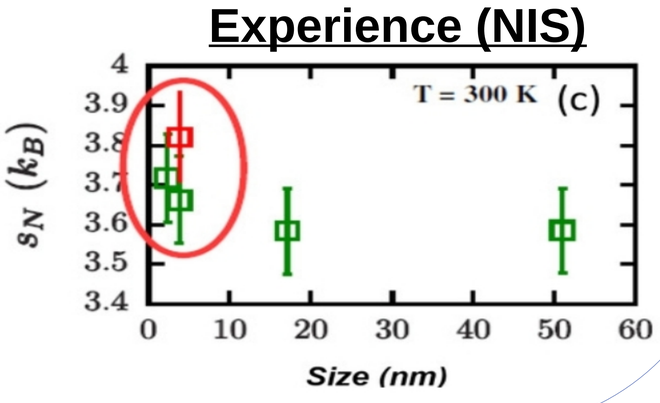
Surface modes



Numerical simulation (MD)



Experience (NIS)



Conclusions

- In comparison with previous numerical investigations, the good order of magnitude for the sound velocity has been obtained in both spin states.
- We show an increase of vibrational entropy in SCO nanomaterials due to surface effects, in good agreement with (NIS) measurements.
- Our study confirms the assumption that in SCO phenomena the change in phase stability taking place at the nanoscale are governed chiefly by surface effects.

References

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[2] G. Molnár, M. Mikolasek, K. Ridier, A. Fahs, W. Nicolazzi, A. Bousseksou. Ann. Phys (Berlin), 531, 10, (2019).
[3] M. Mikolasek, W. Nicolazzi, F. Terki, G. Molnár, A. Bousseksou. Phys. Rev. B, 96, (2017).

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