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Computing Thermo-Elasticity of Crystalline Systems from Quasi-Static and Quasi-Harmonic Approximations

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An effective algorithm for the calculation of the thermo-elasticity of solid compounds is discussed and implemented into the CRYSTAL program, a quantum-mechanical ab-initio simulation software (www.crystal.unito.it). The computational approach to the characterization of advanced properties of materials is becoming a powerful complementary tool to actual experiments in the laboratory because of its increasing accuracy and efficiency. The term thermo-elasticity means the thermal dependence of the elastic response of the system. More precisely, speaking about crystalline materials, we should talk about anisotropic thermo-elasticity. This explicitly refers to the ability of characterizing the directional elastic properties and not just their average values - that would be sufficient for isotropic media, such as fluids or amorphous solids.

First of all, the athermal elastic response of a system should to be introduced. It is well known that for the mono-dimensional system – such as a simple spring - its elasticity can be described by the Hooke's Law, in which the elastic constant is a plain scalar describing the linear relationship between the applied strength and observed elongation. By making use of Tensor Algebra, it is possible to extend this law so that the same concepts can be applied to three-dimensional continuous media as well. Specifically, the elasticity of solid compounds has to be expressed in terms of the fourth-order stiffness tensor. Its elements - the elastic constants – define the directional linear relationships between the stress (the forces that the material is experiencing per unit of area) and the strain (deformation per unit of length). Thanks to the symmetry (both intrinsic into the elastic property itself and particular of the given crystal) only a few of the components of this tensor are actually independent and have to be computed.

Then, as the second topic, the thermal effects on solid compounds have to be discussed - especially from the Quantum-Mechanical point of view. In this respect, owing to its high accuracy and modest computational costs, the Density Functional Theory (DFT) arguably represents the method of choice for systems of small to medium size and complexity [1]. Since we are speaking about solids, the only degrees of freedom involved are the vibrational ones. In the last decades, this phenomenon has mainly been treated by means of standard harmonic lattice dynamics. However, when anharmonic thermal effects are totally neglected, the volume and elastic response do not exhibit any dependence on the temperature [2]. An easy way to overcome these limitations is offered by the so-called quasi-harmonic approximation: it is based on the assumption that the harmonic approximation holds for every value of the volume, which is to be viewed as an adjustable parameter [3]. That is, by introducing the explicit volume dependence into the expression of phonon frequencies, the harmonic expression for the Helmholtz free energy can be retained. The point is that it is then expressed as function of both volume and temperature (and not just of temperature as it would be at the harmonic level). By minimizing this function for a given temperature, it is possible to determine the corresponding equilibrium volume. Therefore, by the repetition of this process at several temperatures, it is possible to determine the thermal expansion of the compound.

In order to properly describe the thermo-elasticity, both the topics of elastic response and thermal effects have to be combined together. In general, the thermo-elastic constants of the compound are given by the second-order derivatives of the energy with respect to the strain, normalized by the volume at that temperature. A few approaches are discussed that make use of different expressions for such energy and volume. As a drastic simplification, it is possible to consider only the static electronic energy and no vibrational motion; despite being computationally very cheap, the resulting elastic constants will not exhibit any dependence on the temperature at all and are therefore completely athermal. The first non-trivial model is represented by the **Quasi-Static Approximation**, which assumes that most of the thermal dependence of the elastic response can be attributed to the thermal expansion of the system only. The electronic static energy is still used to compute the energy derivatives, but the equilibrium volume at any given temperature is now considered. A further refinement can be obtained by fully applying the **Quasi-Harmonic Approximation** to the elasticity expression, so that - in addition to the thermal expansion – the Helmholtz free energy (which does take into account thermal contributions for vibrations) is employed to perform the derivatives [4]. Being an explicit treatment of the lattice dynamics, this approach is of course much more expensive than the previous ones; It is however able to provide better results, especially about some fine effect such as the anisotropy of the thermo-elasticity.

We studied the Forsterite mineral which has an orthorhombic lattice, unit formula Mg2SiO4 and space group Pbnm [5]. There are therefore 9 independent elastic constants that have to be determined. We have chosen a non-trivial system because we wanted a medium-complexity test case for our algorithm. At first, the thermal expansion of the Forsterite has been determined by making use of several DFT functionals - characterized by different cost and accuracy. The general conclusion is that different functionals provide different absolute values but their description of the thermal dependence - the trend - is extremely consistent and very close to the experimental data. Then our newly-implemented algorithms have been employed in order to compute the thermo-elastic constants (Figure 1). As for the Quasi-Static Approximation, we found that the thermal effects have been partially underestimated – indeed, the contribution due to vibrational energy is still neglected in this model. Instead, a full Quasi-Harmonic Approximation is able to provide excellent results: the predicted thermal dependence is in excellent agreement with experimental data – especially in the trend.

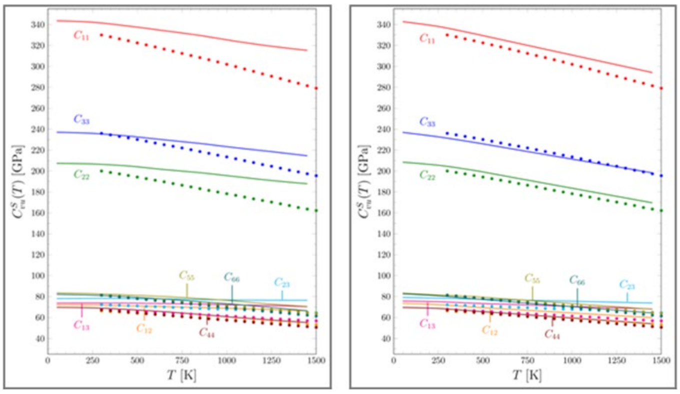

Fig.1.Thermal dependence of the elastic constants of the Forsterite mineral. Computed values are represented as solid lines (Quasi-Static Approximation on the left, Quasi-Harmonic on the right) and are compared to experimental values, represented by bullets.

References:

[1] J. Hafner, C. Wolverton and G. Ceder, Toward Computational Materials Design: The Impact of Density Functional Theory on Materials Research, MRS Bulletin, 31(9), 659-668, 2006

[2] A. Erba, A. Mahmoud, D. Belmonte, and R. Dovesi High pressure elastic properties of minerals from ab initio simulations: The case of pyrope, grossular and andradite silicate garnets, J. Chem. Phys., 140:124703, 2014.

[3] A. Erba, On combining temperature and pressure effects on structural properties of crystals with standard ab initio techniques. J. Chem. Phys. 2014, 141, 124115.

[4] G. F. Davies. Effective elastic moduli under hydrostatic stress–I. quasi-harmonic theory J. Phys. Chem. Solids, 35(11):1513-1520, 1974.

[5] M. Destefanis, C. Ravoux, A. Cossard, A. Erba Thermo-Elasticity of Materials from Quasi-Harmonic Calculations. Minerals 2019, 9, 16.