Thermo-Elasticity of Molecular Crystals from Quasi-Harmonic Lattice Dynamics: The Case of Copper(II) Acetylacetonate

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Abstract

A computationally affordable approach is presented for the quantum-mechanical calculation of thermo-elastic moduli of molecular crystals. The methodology relies on the description of the thermal expansion of the material, as obtained from quasi-harmonic lattice-dynamics. The thermo-elastic response of the metal-organic copper(II) acetylacetonate molecular crystal is investigated. Comparison with experimental data at room temperature shows how the mechanical properties obtained from standard static calculations at the absolute zero of temperature can be off by up to 100%. Moreover, present results show how the anisotropy of the elastic moduli can be significantly affected by the thermal expansion.

Keywords:

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Thermo-elasticity represents the dependence of elastic mechanical properties of materials on temperature. In particular, the thermo-elastic response of crystalline materials is described by the thermal dependence of all the isothermal or adiabatic elastic constants defining the fourth-rank elastic tensor, which provides the formal description of the anisotropic mechanical properties of the material in the elastic regime [1].

The accurate description of thermo-elasticity is relevant to many areas of research including i) geophysics, where the elastic properties of minerals at temperatures of the Earth mantle determine the velocity of propagation of seismic waves [2–5]; ii) refractory materials, whose mechanical stiffness must not be deteriorated at high temperature [6–9]; iii) pharmacology, where most potential drugs are synthesized in the form of molecular crystals, whose mechanical stability at room temperature is crucial for an effective tableting process [10–15]; iv) catalysis, where the mechanical instability of porous frameworks poses serious limitations to their effective use, as for metal-organic frameworks [16–18].

There is great interest in the possibility of describing the thermo-elasticity of materials from quantum-mechanical simulations. While calculations based on the density functional theory (DFT) have proved reliable in the prediction of many static properties of materials in the last decades, the effective inclusion of thermal effects still represents a challenge to state-of-the-art methodologies, particularly so when one needs to go beyond the usual harmonic approximation in the description of the lattice dynamics [19–21]. For instance, this is the case when i) cubic interatomic force constants are needed to compute phonon lifetimes and the thermal lattice conductivity; and ii) the free energy dependence on volume and strain is needed to determine thermal expansion and thermo-elasticity. While the former class of physical properties above requires the explicit evaluation of anharmonic terms of the nuclear potential [22–28], the latter has often been tackled within the so-called quasi-harmonic approximation (QHA), as long as inorganic solids were considered [29–32].

Owing to the progresses made in the inclusion of dispersive interactions into the DFT and in the exploitation of parallel computing, only very recently the QHA could be effectively applied to organic molecular crystals and mixed organic-inorganic materials such as metal-organic frameworks to determine their thermal expansion [33–40]. Let us stress that while the evaluation of the thermal expansion of the system requires the calculation of the dependence of the free-energy on volume, the evaluation of the thermo-elasticity involves the extra dependence of the free-energy on strain, which makes the corresponding lattice dynamical

calculations much more demanding and challenging, particularly so for soft materials with low-frequency phonon modes.

In this Letter, we introduce an affordable quasi-harmonic computational protocol for the description of the thermo-elasticity of molecular crystals within the framework of dispersion-corrected DFT calculations. We apply our scheme to the investigation of the thermo-elasticity of the metal-organic copper(II) acetylacetonate molecular crystal: a system that has recently attracted a lot of attention because of its unusual high flexibility [41]. The present quantum-mechanical calculations allow to report the first complete characterization of the 3D anisotropic elastic response of this system, as well as its thermal evolution. Inclusion of thermal effects up to room temperature results in dramatic changes of the statically computed values. Comparison with the experimentally measured values of the Young modulus along two crystallographic directions confirms the reliability of the description to an unexpected degree.

Isothermal elastic constants are second free-energy density derivatives with respect to pairs of strain types:

$$C_{vu}^{\mathrm{T}}(T) = \frac{1}{V(T)} \left[\frac{\partial^2 F}{\partial \eta_v \partial \eta_u} \right]_{\boldsymbol{\eta}=\mathbf{0}} , \tag{1}$$

where $V(T)$ is the equilibrium volume of the system at temperature T, F is the Helmholtz free energy, η_v is one of the six independent components of the strain tensor $\boldsymbol{\eta}$, and $v, u = 1, \ldots, 6$ are Voigt indices [42]. The calculation of thermo-elastic coefficients from Eq. (1) is a formidable computational task for systems with more than a few atoms per cell and characterized by a low crystallographic symmetry [32]. Indeed, it requires the explicit knowledge of how the free energy depends on strain. Here, we introduce a different strategy where thermo-elastic constants are obtained from:

$$C_{vu}^{\mathrm{T}}(T) \simeq \frac{1}{V(T)} \left[\frac{\partial^2 E}{\partial \eta_v \partial \eta_u} \right]_{\boldsymbol{\eta}=\mathbf{0}} . \tag{2}$$

While Eq. (2) still relies on the quasi-harmonic determination of $V(T)$, now the second energy derivatives with respect to strain are evaluated on the static internal energy E and not on the free energy F, and this dramatically simplifies the corresponding calculations. Our methodology consists of the following steps:

1. The structure is fully relaxed in the athermal limit by minimizing the static internal energy E;

2. The thermal expansion $V(T)$ of the system is computed from a standard quasi-harmonic procedure, where harmonic vibration frequencies are computed at different volumes. At each volume, the structure is relaxed by means of a volume-constrained optimization on the static energy E, which allows to take into account most anisotropic effects on the structure;

3. At each desired temperature T, the thermo-elastic constants are computed from Eq. (2) starting from the corresponding equilibrium structure determined at the previous point.

We stress that the algorithm we just sketched introduces some further approximations with respect to the full quasi-harmonic treatment. In particular, the structural anisotropy of the thermal expansion is obtained from static energy minimizations, as well as the energy dependence on strain. A more explicit description of the structural anisotropy is possible, based on free energy minimizations instead [43, 44]. These simplifications prove essential for the applicability of the quasi-harmonic methodology to organic and metal-organic materials.

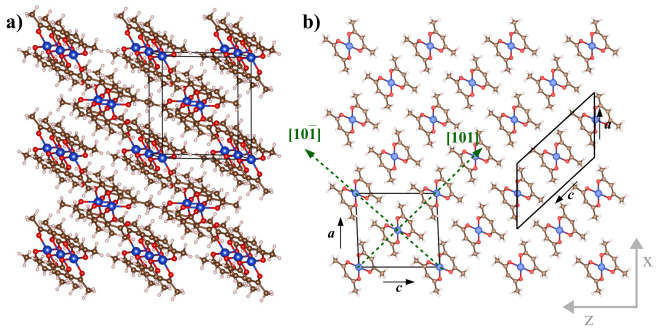


FIG. 1: a) Atomic structure and $P2_1/n$ lattice cell of copper(II) acetylacetonate crystals; b) atomic structure of copper(II) acetylacetonate crystals in the **ac** crystallographic plane. The two directions along which the elastic Young modulus of the system has been experimentally determined are identified by green arrows.

Calculations are performed with the CRYSTAL program for quantum-mechanical simulations of the condensed matter [45, 46]. The hybrid PBE0 exchange-correlation functional is used [47] as corrected for missing dispersive interactions with Grimme's D3scheme [48, 49]:

PBE0-D3. A basis set of triple-zeta quality plus polarization is used [50]. Reciprocal space is sampled on a Monkhorst-Pack mesh with a shrinking factor of 2.

The copper(II) acetylacetonate molecules are planar and crystallize in a monoclinic lattice that can be described with different cells. Figure 1 a) shows the stacking of the molecules in the lattice along the **b** lattice vector, and the shape of the $P2_1/n$ lattice cell used in Ref. [41]. Figure 1 b) shows the structure of the crystal in the **ac** crystallographic plane. Green dashed arrows identify the two crystallographic directions along which the Young modulus has been measured experimentally by Worthy *et al.* [41]. The two directions are [101] and $[10\bar{1}]$ and are expressed in terms of the **a** and **c** lattice vectors of the $P2_1/n$ cell in the left. The figure also shows how the two directions are oriented relative to the $P2_1/c$ cell used instead in our calculations, in the right.

The first step of our methodology consists in a standard QHA calculation to determine the thermal expansion of the system. Harmonic vibration frequencies have been computed at four volumes, from a -2.5% compression to a +5% expansion relative to the static optimized equilibrium volume. Harmonic frequencies as a function of volume are then fitted to a quadratic polynomial function and the fitting coefficients used to set up the canonical vibrational partition function and compute the Helmholtz free energy $F(V;T)$ on a dense

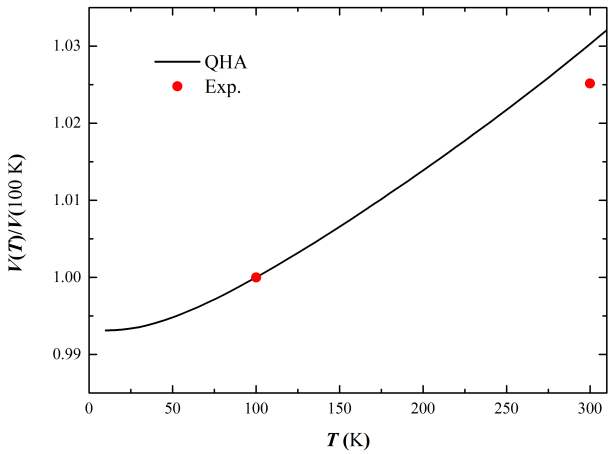
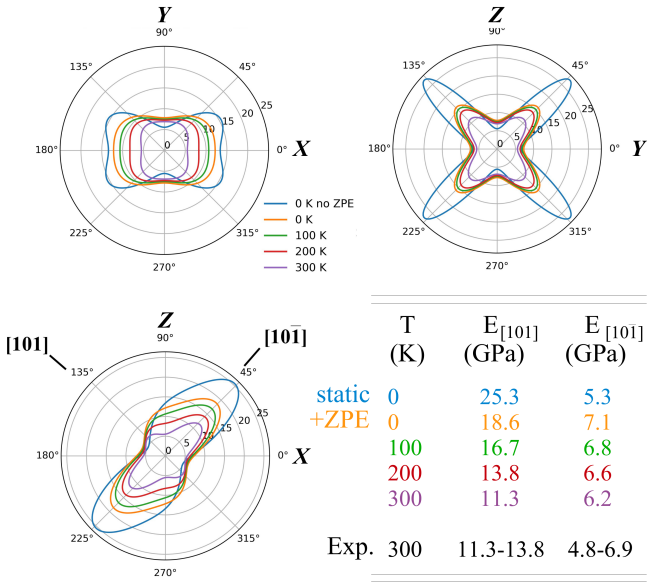


FIG. 2: Volumetric thermal expansion of copper(II) acetylacetonate crystals in the 0-310 K temperature range. Available experimental data (red squares) are from Ref. [41]. The black line is the expansion obtained from our QHA calculations.



	T (K)	$E_{[101]}$ (GPa)	$E_{[10\bar{1}]}$ (GPa)
static	0	25.3	5.3
+ZPE	0	18.6	7.1
	100	16.7	6.8
	200	13.8	6.6
	300	11.3	6.2
Exp.	300	11.3-13.8	4.8-6.9

FIG. 3: 2D plots of the Young modulus (in GPa) of copper(II) acetylacetonate crystals in three planes (XY, YZ and XZ) and at four temperatures (0, 100, 200 and 300 K). The directional Young modulus at 0 K is computed both without and with inclusion of the zero-point energy (ZPE). The XZ plane is the one displayed in Figure 1 b). The table in the bottom-right corner of the figure reports the thermal evolution of the computed Young modulus along the two crystallographic directions, [101] and [10$\bar{1}$], probed in the experiments in Ref. [41].

grid of volumes at each desired temperature. The $V(T)$ relation is obtained by minimizing the free energy with respect to volume at several temperatures [51–54]. The computed volumetric thermal expansion $V(T)$ is reported in Figure 2 (black line) where it is compared with available experimental data (red squares) from Ref. [41]. The agreement between the two sets is remarkable, which proves that the QHA provides a reliable description of the thermal expansion in this case. The metal-organic molecular crystal of copper(II) acetylacetonate is found to expand by 1.7% just by inclusion of zero-point motion effects at the absolute zero, which is followed by a further thermal expansion of about 4% when temperature is raised from 0 to 310 K.

Starting from the thermal expansion determined by the QHA, isothermal elastic constants have been computed through Eq. (2) at four different temperatures: 0, 100, 200 and 300 K.

At the absolute zero, two sets of elastic constants have been evaluated, one corresponding to the equilibrium volume obtained from the standard static geometry optimization, and one corresponding to the equilibrium volume at 0 K upon inclusion of zero-point motion effects. Once the full set of elastic constants is obtained, a variety of mechanical features of the material can be derived such as the bulk modulus, the shear modulus, the Young modulus, Poisson's ratio, the velocity of propagation of directional elastic waves, etc. In particular, the directional Young modulus can be determined, which measures the stiffness of the material along any direction in space [42, 55]. The thermal evolution of the Young modulus of copper(II) acetylacetonate crystals is shown in Figure 3 where it is reported in 2D maps in three Cartesian planes (XY, YZ and XZ). The following can be observed: i) as expected, the mechanical stiffness decreases with temperature (i.e. the Young modulus decreases); ii) the Young modulus does not shrink isotropically with temperature and rather the anisotropy of the mechanical response significantly evolves as temperature changes. For instance, let us have a closer look at the spatial dependence of the Young modulus in the YZ plane. While the Young modulus almost does not change along the Y axis (with values close to 6 GPa at 0 K and 300 K), its value passes from 27 GPa to 11 GPa in the same temperature range in the diagonal YZ direction. A more quantitative analysis on the thermal evolution of the computed Young modulus is provided in the table in the bottom right corner of Figure 3, where the two crystallographic directions in the **ab** plane, [101] and [10$\bar{1}$], are considered, which were graphically marked by the green arrows in Figure 1 b). These are the only two directions along which the Young modulus of copper(II) acetylacetonate crystals has been experimentally measured [41]. Also in this case, along one direction, [10$\bar{1}$], the Young modulus shows little thermal evolution while along the second one, [101], it changes from 25.3 GPa at 0 K in the static limit to 11.3 GPa at 300 K. The comparison with the experimental values shows that it is absolutely mandatory to take into account thermal effects to accurately reproduce the room temperature mechanical features of this class of metal-organic molecular crystals and, at the same time, that the simplified quasi-harmonic scheme introduced here provides a feasible way to do so.

The evolution with temperature of the mechanical stiffness of copper(II) acetylacetonate crystals is shown even more explicitly in Figure 4, where a 3D representation of the spatial dependence of the Young modulus is reported. The figure clearly shows how, still down to the

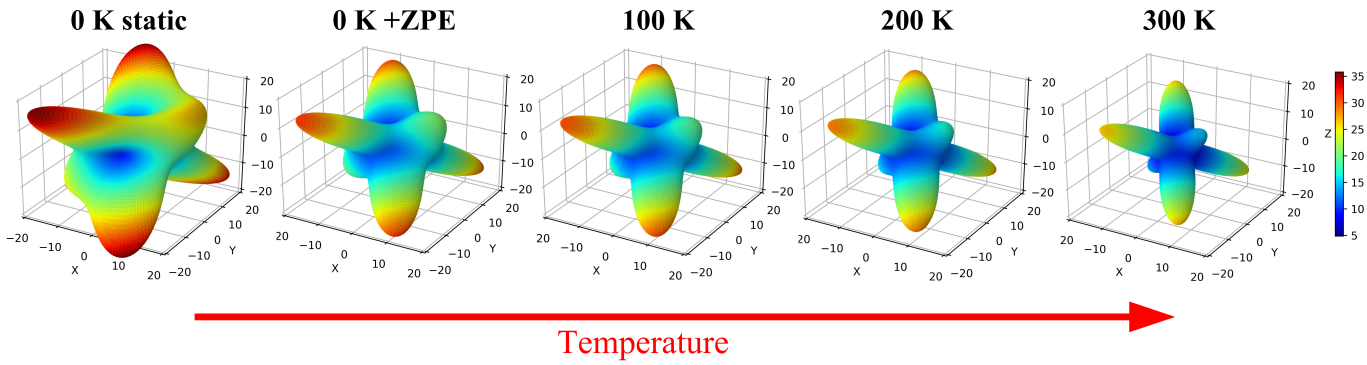


FIG. 4: 3D plots of the spatial distribution of the Young modulus of copper(II) acetylacetonate crystals as a function of temperature. Data are in GPa.

absolute zero of temperature, the large expansion of about 1.7% due to the lattice-dynamical zero-point motions produces a sizable modification to the elastic mechanical response of the system. Both the magnitude of the stiffness and the anisotropy of its spatial distribution are significantly affected by the expansion. As temperature increases from 0 to 300 K a further volume expansion by about 4% is observed, which is again reflected in the thermo-elastic features of the crystals.

In conclusion, we have shown how sensitive to temperature the mechanical response of metal-organic molecular crystals is. In particular, the thermo-elastic behavior of the monoclinic crystals of copper(II) acetylacetonate does not reduce to an isotropic shrinking of the Young modulus, and is instead characterized by a rather anisotropic evolution. Furthermore, we introduce a simplified quasi-harmonic approach, based on the explicit description of the lattice dynamics as a function of volume, which makes this type of thermo-elastic simulations feasible on metal-organic materials from quantum-mechanical calculations.

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