High-pressure and High-temperature Properties of Solids from Quantum-mechanical Calculations: The Implementation of Fully-automated Algorithms into the CRYSTAL Program

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An overview is given of most of the algorithms which have been devised in recent years for the *ab initio* description of structural, elastic and thermodynamic properties of solids (under high pressure and/or at finite temperature), as implemented into the public CRYSTAL program [1]. The strategy that has been followed in their implementation is based on the maximization of their user-friendliness thanks to their fully-automated character: a single-run calculation is required to compute each of the properties to be listed below, activated by a single keyword, where no additional parameters have to be specified unless desired (*i.e.* default values have been optimized for each of the algorithm-specific numerical parameters) [2].

The *P-V* relation is computed both via a numerical volume-constrained equation-of-state (EOS) approach and via an analytical pressure-constrained stress-tensor approach [3]. The fourth-rank elastic tensor components are computed as numerical first-derivatives of analytical energy gradients by taking full advantage of the point-symmetry of the crystal [4]. Both harmonic and quasi-harmonic lattice-dynamical calculations are performed to simulate thermodynamic properties, the thermal expansion coefficient, the *P-V-T* EOS, the thermal dependence of the bulk modulus, and to combine pressure and temperature effects [5-9]. Solid solutions are modeled following a supercell approach, where symmetry-irreducible configurations are counted via Polya's theorem and determined via a Monte Carlo sampling [10].

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