The ground state elemental crystals as a benchmark set for solid state DFT: intrinsic accuracy and code comparison

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ABSTRACT A central issue when applying DFT for property predictions is an assessment of the error bars on the computed quantities. These are usually determined by performing calculations for a set of experimentally well-known benchmark systems. For molecules, some commonly accepted test sets are available for the evaluation of various properties at various levels of theory. Similar systematic and broad tests for crystalline solids are not that easily found. Therefore, several basic properties have been computed for a test set with all ground state elemental crystals (excluding most lanthanides). This test set contains many different elements, crystal structures and chemical bond types in a natural way. Three general-purpose DFT codes are employed, using a PBE functional. The following table summarizes a comparison between VASP results and experiment. Both the systematic deviation of the DFT numbers and the remaining error bars are presented.

	deviation	error bar
cohesive energy ΔE_{coh} [kJ/mol]	$-0\,\%$	16
equilibrium volume V_0 [Å^3/atom]	$+4\,\%$	0.6
equilibrium bulk modulus B_0 [GPa]	$-5\,\%$	9
pressure derivative of B_0 [–]	$+6\,\%$	0.5
elastic moduli C_{ij} [GPa]	$-2\,\%$	6
melting temperature T_m [K]	$-5\,\%$	167

Although the better part of the error bars stems from the choice of a particular DFT functional, a sometimes non-negligible part of it is due to implementation issues. The same test set of elemental crystals can provide insight into this aspect as well. By directly comparing the DFT equations of state for different codes, a quality factor Δ can be defined. This quantity expresses the rms energy deviation between the $E(V)$ curve of a code under test, and that of the APW+lo code WIEN2k, averaged over the entire test set. WIEN2k is an all-electron method, believed to provide results that are as close as possible to the true results for the chosen functional. VASP is found to have a Δ of 2 meV, while for GPAW, a similar grid-based code, it is 4 meV.

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