

Structural Paths for the High-Pressure Phase Transitions of AgI
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First-principles calculations with Density-Functional-Theory (DFT) Hamiltonian and localized basis set (CRYSTAL code [1]) were performed on AgI, showing that it transforms from the cubic zinc blende to the tetragonal anti-litharge structure at 1.2 GPa, and then to cubic rocksalt at 1.6 GPa, in agreement with experiment [2]. For both reconstructive phase transitions, a monoclinic Pm pathway was considered and tested by computing the enthalpy profile (with full structural optimization) vs. the order parameter, according to a previously presented method [3]. On the basis of the activation enthalpies obtained, a bifurcated three-step kinetic mechanism is proposed. One step relates the anti-litharge structure to a metastable orthorhombic $Bmm2$ phase which appears along the transformation path. Then two alternative steps follow, transforming the intermediate phase into either zinc blende or rocksalt. The enthalpy curve along the Pm pathway shows two bottle-neck states bracketing the metastable phase, with a predicted maximum activation enthalpy of 0.088 eV. The mechanism is characterized by changes of the Ag coordination number from 4 (zinc blende and anti-litharge) to 5 ($Bmm2$ phase) to 6 (rocksalt), which account for the dependence of the unit-cell volume on the order parameter.

[1] Saunders V.R., et al., *CRYSTAL03: User's manual*, 2003, University of Torino, Italy, and CLRC Daresbury Laboratory, UK. [2] Keen D.A., Hull S., *J. Phys.: Condens. Matter*, 1993, **5**, 23. [3] Catti M., *Phys. Rev. Lett.*, 2001, **87**, 035504.

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