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 \( P_m \) 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 \( B_{mm2} \) 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 \( P_m \) 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 (\( B_{mm2} \) phase) to 6 (rocksalt), which account for the dependence of the unit-cell volume on the order parameter.


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