Quantum mechanical simulation of pressure induced polymorphism in AgCl

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High pressure experiments in silver halides have recently identified non-cubic structures in their pressure induced polymorphic sequence connecting the B1 and B2 phases [1]. Most surprisingly, those same structures have been also found as intermediates [2] along proposed B1-B2 mechanisms in alkali halides. These facts have drawn us to undertake a detailed study of the thermodynamic and mechanistic aspects of the polymorphic sequence of AgCl, which includes monoclinic (KOH-type) and orthorhombic (TlI-type) phases. The electronic structure has been determined in the framework of the DFT as implemented in VASP [3]. Thermodynamic results are promising due to their good agreement with a number of observable properties. On the one hand, these results allow us to extend the limited experimental knowledge of the AgCl response to hydrostatic pressure. A non-expected energetic quasi-degeneration has been found for the TlI-type and anti-TlI-type structures. On the other hand, this agreement allows us to go one step further, and try to determine the involved transition paths. Different approximations (complete and partial interpolations, as well as full optimizations) have been dealt with in order to study the cell changes under the maximal common subgroup ($P2_1/m$). Historical reasons have also animated us to explore the virtual B1 to B2 $R3m$ energy surface (Buerger mechanism). Shocking results have been obtained: the appearance of several relative minima in the Gibbs energy profile of AgCl in contrast with a path without intermediates found in alkali halides. This feature is probably related, as well as the existence of non-cubic structures in the polymorphic sequence, to the partially covalent nature of the chemical bonds.

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