Comment on "Orthorhombic Intermediate State in the Zinc Blende to Rocksalt Transformation Path of SiC at High Pressure"

In Ref. [1], an orthorhombic transformation path (TP) was proposed for the high pressure tranformation of SiC between zinc blende and rocksalt structures. The intermediate state was described as having orthorhombic $Pmm2$ symmetry and its enthalpy barrier was calculated using first principles methods. The energy barrier was found at high pressures to be much smaller than the previously proposed pathway of symmetry $R3m$ [2]. Apparently, no systematic symmetry considerations were used in the search of this alternative TP. It was established from the reinterpretation of the results of a molecular dynamics study done using empirical interatomic potentials [3]. We want to point out in this Comment that the possible TPs for a reconstructive phase transition, as that of SiC, can be systematically derived using group theory, along the lines suggested in Ref. [4]. The orthorhombic TP proposed in Ref. [1] is, in fact, readily derived within this approach, but its symmetry should be correctly labeled as $Imm2$.

The usual smoothness of the energy landscape makes highly probable that the lower energy/enthalpy paths correspond to high-symmetry configurations, which are necessarily energy extrema with respect to many degrees of freedom. One can then consider as most probable intermediate states for the transformation those having higher symmetries compatible with a continuous evolution between the initial and final states. This reduces the search to configurations with space groups having as supergroups both the initial and final space groups, and fulfilling the additional condition that the occupied Wyckoff orbits are equivalent when descending the symmetry to the common subgroup from either the initial or the final phases. We have performed this search for the transition of SiC using the group-theoretical tools available in the Bilbao Crystallographic Server [5]. Descending up to a second step along the chain of maximal subgroups of F-43m, only three symmetries fulfill the mentioned conditions, namely, $R3m$ (4), $Imm2$ (6), and $P2_13$ (8) (the indices of the subgroups with respect to F-43m are indicated in parentheses; those with respect to the rocksalt space group Fm-3m are just doubled, forced by the *Wyckoff-match* condition mentioned above). The TP $R3m$ was the first one proposed in the literature [2]. The third path $P2_13$ was also mentioned in Ref. [2], but discarded through qualitative sterical arguments. The orthorhombic TP $Imm2$ apparently differs from the $Pmm2$ pathway claimed in Ref. [1] as the most favorable energetically. But, in fact the intermediate states considered in this reference maintain an overlooked body-centering translation. This means that the actual most favorable pathway shown in Ref. [1] has indeed $Imm2$ symmetry, in accordance with a derivation from general symmetry arguments. Actually, such a $Imm2$ path had already been suggested in Ref. [6] using sphere-packing considerations. This correction extends also to subsequent publications [7].

In conclusion, we stress that possible TPs for reconstructive phase transitions can be readily generated and classified in a systematic manner using group-subgroup relations among space groups, and the corresponding relations of the Wyckoff positions [4], which are freely available [8] (see also the very recent Ref. [9]). The TPs of highest possible symmetry can be taken as the most probable ones. This approach efficiently limits the possible paths to be considered. In the above case, up to three TPs are found competitive, but, for instance, for the wurtzite to rocksalt transition the same symmetry arguments yield only (up to the same level of symmetry reduction, i.e., second level in the chain of minimal subgroups of wurtzite) a single TP, namely, an orthorhombic $Cmc2_1$ path (of index 3 with respect to wurtzite space group $P6_3mc$). This pathway is, in fact, the one that has been recently proposed, either from *ad hoc* considerations [10] or using sphere-packing arguments [11].

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