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First-principles calculation of P-T phase diagram of boron nitride

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Abstract – We present a comprehensive investigation on the lattice dynamic and thermodynamic properties of all the known BN phases and polytypes by the first-principles linear-response calculation in the framework of density-functional perturbation theory. Based on the calculated results, we are able to establish the exact thermodynamic relationships for Gibbs free energy, pressure and temperature of the system theoretically. Finally, the relative structure stabilities and P-T phase diagram of BN phases on temperature and pressure are explored.

Boron nitride is being attracted many research efforts for its extraordinary properties in mechanics, thermodynamics and electronics. As a man-made material, boron nitride doesn't exist in nature. Up to now, the compound has been synthesized in several forms. The first BN compound was preparing by Balmain in 1842 [1]. It is a kind of white powder of hexagonal graphite-like crystal. Since then, this hexagonal BN (h-BN) has generally been being used as the starting material to synthesize the other phases of the compound. Wentorf successfully synthesized cubic BN (c-BN) in zincblende structure from h-BN under high pressure (HP) and high temperature (HT) condition in 1957 [2]. Later, the hexagonal wurtzite BN (w-BN) was detected as an intermediate product in the process of HP-HT c-BN synthesis [3].

The largest crystal size of the fabricated BN is no more than a few millimeters so far, which is greatly limited the industrial application of the material. Thus, it has been being constantly a main effort for how to synthesize a bigger bulk in the research. The thermodynamic condition is an important factor in the compound's synthesis and is subjected intensive investigations.

Our calculations were carried out using the ABINIT code [4] based on plane-wave pseudopotential approach in the framework of density-functional theory and density-functional perturbation theory. The pseudopotentials have been generated as single projector, ordinary norm conserving, based on the Troullier-Martins method. The second derivatives of total energy and dynamic matrices for a set of minimum non-symmetrical q-points are calculated firstly. The real-space interatomic force constant matrix is calculated by the backward Fourier transformation of these full-set q×q×q dynamic matrices. The dynamic matrix for an arbitrary **q** vector can be conveniently constructed using the obtained real-space interatomic force constant matrix [5]. The lattice dynamic and thermodynamic properties of all the reported BN phases and polytypes are investigated thoroughly. Based on these thermodynamic data, the exact thermodynamic relationships for Gibbs free energy, pressure and temperature of the system are established theoretically. Then, we investigate the relative structure stabilities of these BN phases. Finally, an *ab initio* P-T phase diagram of BN is suggested.

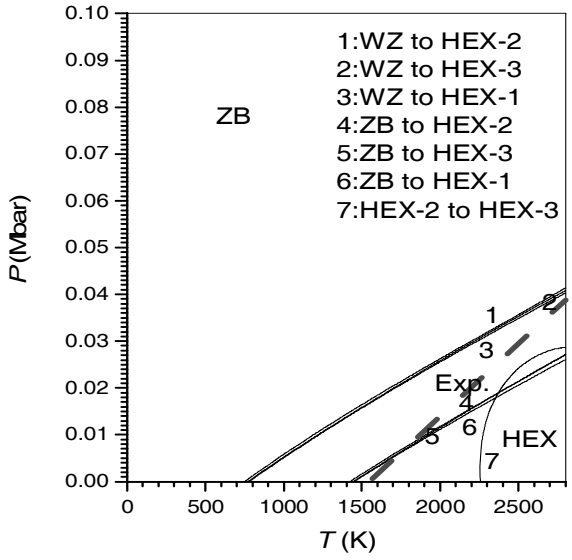

Figure 1: ab initio P-T phase diagram of boron nitride. The thick dashed line shows the experimental result.

References

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[3] F. P. Bundy, R. H. Jr. Wentorf , J. Chem. Phys. 38 (1963) 1144.
[4] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated (URL http://www.abinit.org).
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