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Ab initio studies on ammonium iodine under high pressure*

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Ammonium iodine (NH_4I) as an important member of hydrogen-rich compounds has attracted a great deal of attention owing to its interesting structural changes triggered by the relative orientations of adjacent ammonium ions. Previous studies of ammonium iodide have remained in the low pressure range experimentally, which we first extended to so high pressure (250 GPa). We have investigated the structures of ammonium iodine under high pressure through *ab initio* evolutionary algorithm and total energy calculations based on density functional theory. The static enthalpy calculations show that phase V is stable until 85 GPa where a new phase *Ibam* is identified. Calculations of phonon spectra show that the *Ibam* phase is stable between 85 GPa and 101 GPa and the *Cm* phase is stable up to 130 GPa. In addition, ammonium iodine dissociates into NH_3, H_2, and I_2 at 74 GPa. Subsequently, we analyzed phonon spectra and electronic band structures, finding that phonon softening is not the reason of dissociation and NH_4I is always a semiconductor within the pressure range.

Keywords: hydrogen-rich compounds, high pressure, phase transition

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1. Introduction

Hydrogen has been a concern for ages due to its potential of being room-temperature superconductor.[1–5] Dias *et al.*[6] have reported metallization of solid H_2 at 495 GPa, however, its reality and difficulty of reaching so high pressure compel us to turn our attention to hydrogen-rich compounds,[7] which are able to metallize at much lower pressures. In recent years, in addition to the breakthrough in H_3S,[8,9] extensive hydrogen-rich compounds with high T_c have been uncovered consecutively, such as LaH_{10}[10,11] and YH_{10}.[12] Nevertheless, ammonium halides as another important member of hydrogen-rich compounds have received much less attention.

Research on structures has always been one of the vital and major scientific tasks, and is also of challenge due to their complexity and diversity. Ammonium halides have been grabbing researchers' eyes owing to their similarity to alkali halides on the one hand and abundant phase transitions involving the relative orientations of adjacent ammonium ions[13] on the other hand. It is well known that there exist five phases in NH_4Br and NH_4I. An ordered tetragonal phase Ⅲ does not exist in NH_4Cl. The others are a disordered NaCl structure (phase I), a disordered CsCl structure (phase Ⅱ), an ordered CsCl structure (phase IV) and a slightly distorted tetragonal CsCl structure (phase V). These have successively been proved experimentally[14–22] and theoretically.[23–25] At room temperature, phase I transforms to phase Ⅱ at about 0.05 GPa with increasing pressure, subsequently a further transition to phase IV with a parallel ordering of ammonium ions occurs at 2.7 GPa.[21] As the pressure increases up to 5.4 GPa,[15] a phase transition to phase V occurs, interestingly the transition is caused by reorientational motions of the NH_4^+ ions in phase IV. Nevertheless, numerous experiments have been conducted to determine the phase transition and to establish the crystallographic structures, such as x-ray,[26] neutron diffraction,[27–31] electron diffraction,[32] Raman,[14,15,17] and infrared studies.[33] Although extensive efforts have been made for NH_4I, the structures, stability and electronic band structures of ammonium iodine at high pressure are still little known. Here we will study them up to 250 GPa at zero temperature.

2. Computational methods

The evolutionary algorithm performed with the USPEX code[34–36] is implemented to explore potential stable structures of NH_4I at pressures 0–250 GPa, which is a potent tool of predicting all thermodynamically stable compounds in the case of given elements. The first generation is generated randomly, then 60% of low-energy structures are passed on to the next generation. The process is terminated after about 40 generations. Our structure relaxations are carried out us-

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ing the density functional theory within the Perdew–Burke–Ernzerhof functional (generalized gradient approximation)[37] and the projector-augmented wave method as implemented in the VASP code.[38,39] A cutoff energy of 900 eV and the Mokhorst–Pack k-points meshes with a reciprocal space resolution of $2\pi \times 0.03$ Å^{-1} are used to ensure that the total energy is well converged to less than 1 meV per atom. We also calculated phonon dispersion curves with the PHONOPY code[40,41] based on a supercell approach with the force-constant matrices. Supercell of each phase contains 100 atoms at least.

3. Results and discussion

3.1. Crystal structures and stability of NH_4I

We performed fixed-composition structure prediction of NH_4I with the cell size containing two, three and four formula units by the *ab initio* evolutionary algorithm up to 250 GPa. There is no doubt that these three phases (Ⅲ, IV and V) have been found and confirmed experimentally by us.[14–22] Still, three novel structures with space group *Ibam*, *Cm* (in Fig. 2) and *P*1 have been uncovered for the first time. Before the pressure reaches 70 GPa, the structures and phase transformation sequence are almost identical to the previous results. We present the enthalpy differences of phases Ⅲ and V (phase IV is the reference) at 0 K in Fig. 1(a), where we can easily see phases Ⅲ and IV existing in narrow pressure ranges, 0–3.3 GPa and 3.3–9 GPa, respectively. Heyns and Hochheimer suggested the transition pressures are 0.45 GPa[14,15] and 4 GPa[14,17] at 100 K by measuring Raman spectroscopy. Balagurov uncovered that phase transition from phase IV to phase V takes place at 8.6 GPa[42,43] from neutron diffraction experiments at room temperature. The discrepancies between the experimental results and our calculated results are distinctly caused by the temperature effect. In addition, Fig. 1(b) shows the enthalpy difference diagram of those mentioned new phases relative to phase V, from which we can see that as pressure is enhanced to 85 GPa, the new phase with space group *Ibam* emerges. When pressure reaches 101 GPa the orthorhombic *Ibam* phase transforms to the monoclinic *Cm* phase. Another phase *P*1 is predicted to emerge above 154 GPa. Due to the dynamic instability, *i.e.*, the phonon frequencies soften to negative value, the *P*1 phase will not be mentioned at all. However, considering the instability of HI[44] and precedent of NH_4Br,[45] we think that NH_4I has the possibility of dissociation under high pressure. Then, we compared the enthalpies of all predicted structures and $NH_3+\frac{1}{2}H_2+\frac{1}{2}I_2$ above 50 GPa, finding that phase V persists up to 74 GPa, where NH_4I dissociates into $NH_3+\frac{1}{2}H_2+\frac{1}{2}I_2$.

As shown in Fig. 2, the $P4/nmm$ and $P\bar{4}3m$ structures have similar configurations, in which iodine ion is located in the body center and surrounded by eight neighbor ammonium ions. In addition, there are four nearest neighbor N–H…I

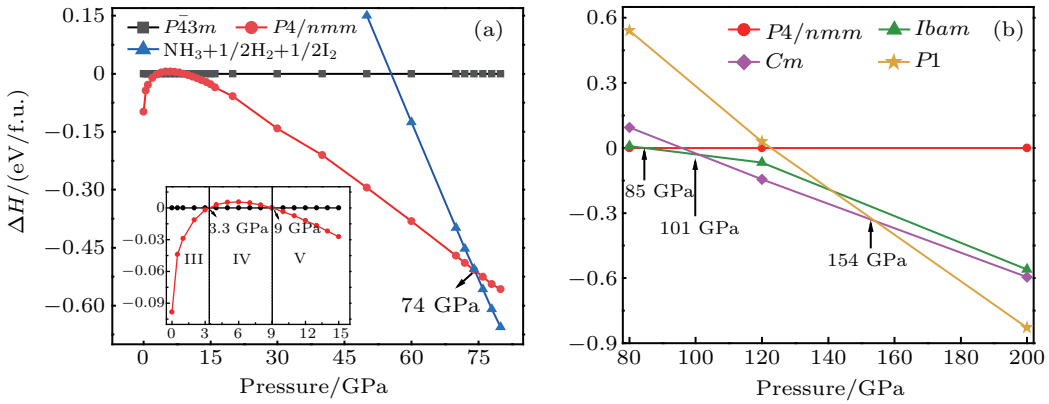


Fig. 1. (a) Enthalpy curves for phases Ⅲ and V (relative to IV phase) as a function of pressure. The inset figures out the transition pressure points from Ⅲ to IV, then to V at 0 K. (b) Enthalpy curves of our predicted phases *Ibam*, *Cm* and *P*1 as a function of pressure (relative to phase V).

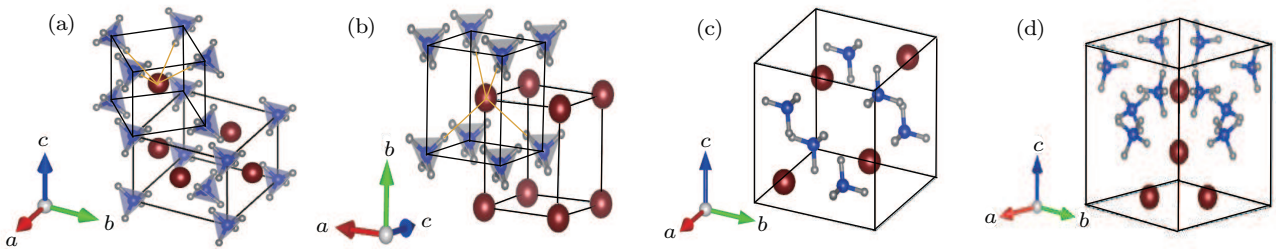


Fig. 2. Structure of NH_4I with space group $P4/nmm$ (phases Ⅲ and V) (a), $P\bar{4}3m$ (phase IV) (b), *Ibam* (c) and *Cm* (d). Ammonium ions take the tetrahedron shape with N^{3-} ion (blue solid ball) at the center and H^+ ion (grey solid ball) at the corner. The red solid balls represent iodine ions.

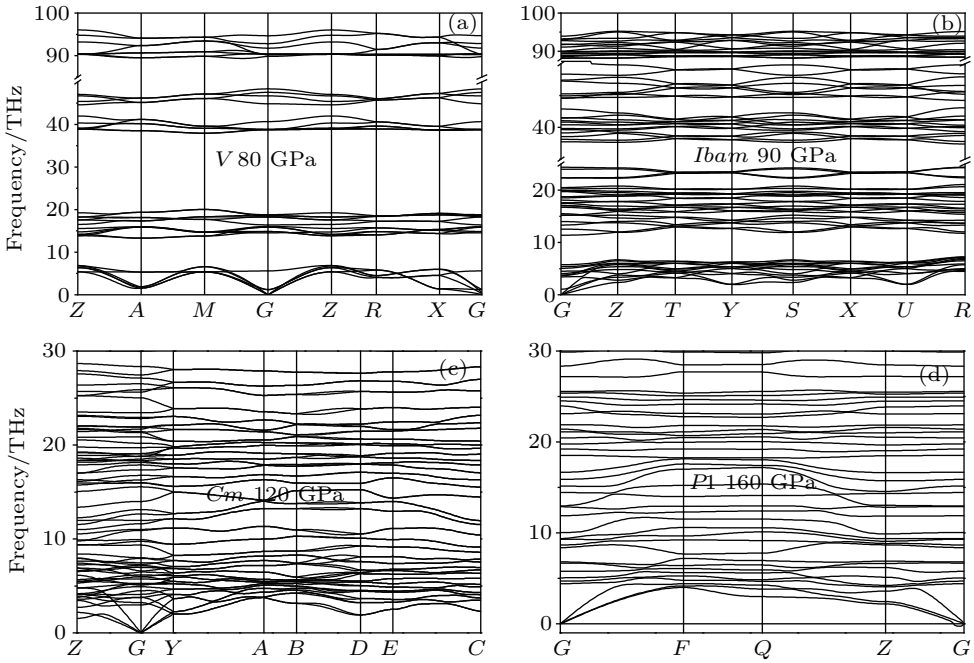


Fig. 3. The calculated phonon dispersion curves of NH_4I for (a) phase V at 80 GPa, (b) the *Ibam* phase at 90 GPa, (c) the *Cm* phase at 120 GPa and (d) the *P*1 phase at 160 GPa.

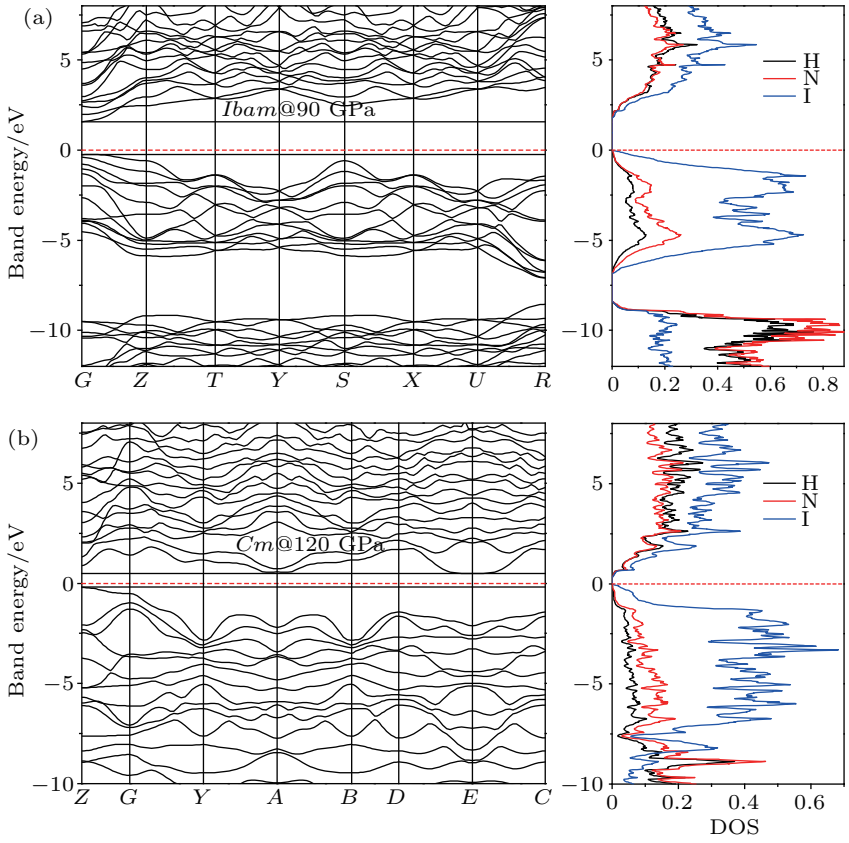


Fig. 4. The electronic band structures and density of states for the *Ibam* phase at (a) 90 GPa and the *Cm* phase at (b) 120 GPa.

bonds in both the structures. However, in the $P4/nmm$ structure the orientation of each ammonium ion is determined by the rotation of its neighbor by 90°, resulting in the four nearest neighbor N–H…I bonds distributing on the same side. In the $P\bar{4}3m$ structure all the ammonium ions have the same orientation so the N–H…I bonds between the ammonium ions pointing directly toward the iodine ion are distributed on the diagonal lines. These prove that the transition is caused by the orientation change of ammonium ions.

We have calculated the phonon dispersion curves of NH_4I along high symmetry directions as shown in Fig. 3. Only the phonon dispersion curves of 80 GPa for phase V, 90 GPa for

Ibam structure, 120 GPa for *Cm* structure and 160 GPa for *P*1 structure are presented here. We can conclude from the calculated results that phase V exists from 9 GPa to 85 GPa, where no imaginary phonon frequency is observed in the whole Brillouin zone, indicating that the $P4/nmm$ structure is dynamically stable. Subsequently, we calculated the phonon dispersion curves of the *Ibam* phase at 90 GPa and the *Cm* phase at 120 GPa and even higher pressures, finding that the *Ibam* phase is dynamically stable from 85 GPa to 101 GPa and the *Cm* phase is stable up to 130 GPa. Nevertheless, the *P*1 phase has been dynamically unstable in the pressure range we studied, because the phonon frequencies soften to negative values.

3.2. Electronic properties of NH_4I

To further study the electronic properties of NH_4I, the electronic band structures and density of states (DOS) are calculated. Here we merely present electronic band structures and corresponding density of states of the *Ibam* phase at 90 GPa and the *Cm* phase at 120 GPa, respectively. An apparent gap is observed in both the band diagrams, implying the character of the semiconductor. In addition, it is at first a direct gap semiconductor, then turns to an indirect gap semiconductor. We also calculated the gap values of phase Ⅲ, IV, V and new phases with pressure in Fig. 5, finding that the gap increases first, as the structure transforms into phase V the value begins to decrease. From the figure of band energy we can see that as pressure is enhanced, the distances among atoms decrease and the hybridization between N and I atoms increases. Furthermore, the conduction band (bottom) moves from the high-energy zone to the low-energy zone gradually, causing the variation of band gap.

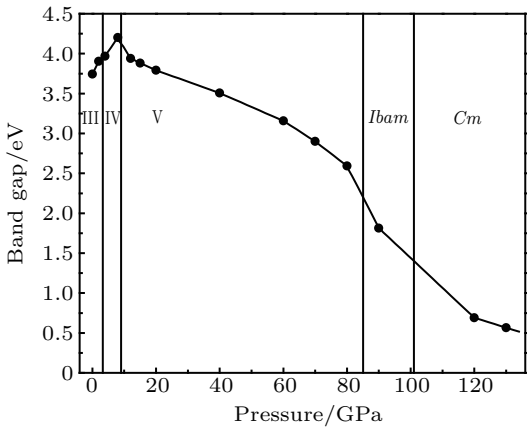


Fig. 5. The calculated band gaps of NH_4I versus pressure.

4. Conclusions

We have searched the structures of NH_4I up to 250 GPa by *ab initio* evolutionary algorithm based on DFT. The novel structures with space groups *Ibam* and *Cm* have been uncovered for the first time. The *Ibam* and *Cm* phases are stable in pressure ranges of 85–101 GPa and 101–130 GPa, respectively. However, considering the instability of HI, we compare the enthalpy values of all predicted structures and $NH_3+\frac{1}{2}H_2+\frac{1}{2}I_2$, and find that phase V dissociates into $NH_3+\frac{1}{2}H_2+\frac{1}{2}I_2$ at 74 GPa. We also verify that the mechanism of Ⅲ–IV to IV–V phase transitions is the NH_4^+ ions rotating 90° around the *c*-axis from the point of microscopic view. The calculations of electronic band structure indicate that it is a semiconductor, and the gap increases first, as the structure transforms into phase V the value begins to decrease.

Parts of calculations were performed in the High Performance Computing Center (HPCC) of Jilin University.

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