High temperature superconducting phase of HBr under pressure predicted by first-principles calculations

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The high pressure phases of HBr are explored with an ab initio crystal structure search. By taking into account the contribution of zero-point energy (ZPE), we find that the $P4/nmm$ phase of HBr is thermodynamically stable in the pressure range from 150 to 200 GPa. The superconducting critical temperature ($T_c$) of $P4/nmm$ HBr is evaluated to be around 73 K at 170 GPa, which is the highest record so far among binary halogen hydrides. Its $T_c$ can be further raised to around 95 K under 170 GPa if half of the bromine atoms in the $P4/nmm$ HBr are substituted by the lighter chlorine atoms. Our study shows that, in addition to lower mass, higher coordination number, shorter bonds, and more highly symmetric environment for the hydrogen atoms are important factors to enhance the superconductivity in hydrides.

I. INTRODUCTION

In 1935, Wigner and Huntington envisioned that, at low temperature, hydrogen molecular would transform into atomic metallic solid hydrogen under 25 GPa.2 Later Ashcroft3 suggested that hydrogen would become a room temperature superconductor under high pressure. After that, tremendous efforts have been invested into the research on the synthesis of metallic hydrogen and its properties, both in theory and experiment.4–14 The mechanism of the superconductivity in metallic hydrogen is believed to be phonon mediated and will be greatly enhanced under high pressure. For instance, the metallic hydrogen in $Cmca$ structure was predicted to have a $T_c$ of 242 K near 450 GPa and would reach higher $T_c$ when hydrogen is compressed into denser structure.14 On the experimental side,13–14,16–18 the experimental observation of the metallic hydrogen is still under debate, and the realization of the superconductivity in solid hydrogen seems to be far away.

Due to the reason that the critical pressure of the metallization of hydrogen is high, it will be difficult to put it into wide applications. Ashcroft15 proposed to metallize hydrogen together with a monatomic or paired metal by using a method of chemical precompression. Since then, compared to hydrogen, a large number of hydrides with superconducting properties at lower pressure have been proposed theoretically and experimentally studied. SiH,16 as a member of IVA hydrides, was predicted to have equivalent electron density compared with pure hydrogen theoretically when compressed to 100 GPa. This compound became the first example of superconducting hydrides in experiment, with a $T_c$ of around 17 K at 96 and 120 GPa.19 Then, quite a few hydrogen-rich compounds were predicted to have high $T_c$ values based on ab initio calculations: SiH$_3$ with $T_c \sim$ 139 K at 275 GPa,19 CaH$_6$ with $T_c$ of about 220-235 K at 150 GPa and so on.19–21

Recently, the sulfur hydrogen system has been identi-
symmetry than the $C2/m$ structure, we believe it is necessary to consider the effect of ZPE in the HBr system.

In this paper, with additional consideration of ZPE, the $P4/nmm$ HBr is found to be more stable than the $C2/m$ phase above 150 GPa. More interestingly, the estimated value of the superconducting transition temperature ($T_c$) of the $P4/nmm$ HBr can get a high value of 73 K (at 170 GPa). Furthermore, we find that an atomic substituted structure of HCl$_{0.5}$Br$_{0.5}$ can realize an even higher $T_c$ of around 95 K at 170 GPa. In addition to the significant effects of low atomic mass, here we reveal that high coordination number, shorter bonds, and a more symmetrically restricted environment of hydrogen atoms play key roles in enhancing superconductivity.

II. METHODS

We used an *ab initio* random structure searching method (AIRSS) to investigate the stable metastable phases of HBr under high pressure up to 200 GPa and different cell-size up to 18 atoms. Structural optimization and electronic structures calculations were carried out by projector augmented wave method implemented in the Vienna *ab initio* simulation package (VASP) Perdew-Burke-Ernzerhof (PBE) and the PBE functional revised for solids (PBEsol) exchange and correlation were employed to investigate the structural stability of HBr, together with Grimmes DFT-D2 method for the van der Waals (vdW) interaction. The plane-wave kinetic cutoff was 400 eV, and the Brillouin zones were sampled by Monkhorst-Pack method with a k-spacing of 0.02 $\times$ 2 $\pi$Å$^{-1}$. ZPE was obtained from the quasiharmonic approximation from phonon calculations, by finite displacement method implemented in PHONOPY code with a $3 \times 3 \times 4$ and $3 \times 3 \times 2$ supercell for HBr with $P4/nmm$ and $C2/m$ phase, respectively. Electron-phonon coupling (EPC) calculations were executed in the framework of density functional perturbation theory, as implemented in the QUANTUM-ESPRESSO code. We adopted a $16 \times 16 \times 20$ k-point mesh for charge self-consistent calculation, a $32 \times 32 \times 40$ k-point mesh for EPC linewidth integration and a $4 \times 4 \times 5$ q-point mesh for dynamical matrix. Norm-conserving pseudopotentials were used with the energy cutoffs of 160 Ry for the wave functions and 640 Ry for the charge density to ensure that the error of total energy was less than 10$^{-6}$ Ry.

III. RESULTS AND DISCUSSIONS

A. Crystal Structure and phase diagram

Neglecting the effect of ZPE, three energy-favorable phases are identified during our crystal structure search. Two of them are stable in enthalpy: the $P - 1$ phase (space group No. 2) below 120 GPa, and the $C2/m$ phase (space group No. 12) above 120 GPa, while the other one, the $P4/nmm$ phase (space group No. 129) is metastable, whose enthalpy is slightly higher than that of the $C2/m$ phase (around 10 meV/atom). The calculated enthalpies are shown in Fig. 1(a). The results given by the two different exchange-correlation functionals show the same tendency. In addition, the functional PBEsol-D2 reduces the enthalpy difference between $P4/nmm$ and $C2/m$ phase, compared with PBE functional. Both the structures and transition pressures are consistent with the previous study.

As mentioned above, ZPE is sometimes crucial to judge the stability of structures for compounds with light elements, it has a more notable effect on high-symmetry structures compared with low-symmetry structures. Due to the fact that $C2/m$ and $P4/nmm$ structures have very different symmetry, ZPE might change their stability sequence. Our calculations presented in Fig. 1(b) show that the $P4/nmm$ phase indeed has lower Gibbs free energy than $C2/m$ phase under high pressure. The Gibbs free energy difference between $C2/m$ and $P4/nmm$ phase becomes larger with the increasing of temperature. Contrary to the earlier report, our calculations suggest that the thermodynamically stable phase of HBr under pressure above 150 GPa is the $P4/nmm$ phase, instead of the $C2/m$ phase. The hydrogen and bromine atoms in the $C2/m$ structure are all two-coordinated and they assemble into 1D chain-like structure, while the hydrogen and bromine atoms in the $P4/nmm$ structure are all four-coordinated and they form a 2D netlike structure. Actually, the $P4/nmm$ and $C2/m$ fulfill a group-subgroup relationship, $C2/m$ is a subgroup of $P4/nmm$ with an index of 4. If we break half of the H-Br bonds in the H-centered tetrahedrons in the $P4/nmm$ structure, the 2D net will break into 1D chains. Then with slight distortion and interlayer sliding, the structure will easily transform into the $C2/m$ structure. This might be the reason why their enthalpy difference at high pressure is so small. Another point that needs to be mentioned is that, due to the 2D and 1D features in the $P4/nmm$ and $C2/m$ structures, and that vdW corrections are crucial to describe 2D and molecular system, the DFT-D2 type of vdW correction is used in this work.

Phonon spectra is often used to verify the dynamical stability of structures. In this case, there is no imaginary frequency for the $P4/nmm$ HBr upon the pressure above 150 GPa, indicating its dynamical stability. Both hydrogen and bromine atoms are monovalent; consequently, they tend to form diatomic molecule and hydrogen bonds between these diatomic molecules. High pressure enhances the atomic orbital overlaps and pushes the molecules to polymerize with each other to form chains or squares, and then further compression leads to symmetrization of the hydrogen bonds. However, in most of the symmetric hydrogen bond cases, the hydrogen atom is two-coordinated, while in the $P4/nmm$ structure, the hydrogen atoms are four-coordinated; that is probably
why it can only appear at such a high pressure above 150 GPa.

FIG. 1: (Color online) The calculated enthalpy of $P4/nmm$ HBr relative to the $C2/m$ HBr under pressure, given by the PBE-D2 and PBEsol-D2 functionals, (a) without and (b) with considering the ZPE, respectively. The inset shows the difference of Gibbs free energy of $P4/nmm$ HBr relative to $C2/m$ phase, with PBE-D2 functional. (c) From $P4/nmm$ HBr to $C2/m$ phase, with bond breaking and interlayer sliding. Once the hydrogen atom moves away from the center of the HBr$_4$ tetrahedron, half of the H-Br bonds in the $P4/nmm$ phase will be broken, which leads to forming a 1D chain-like structure.

B. Electronic structures

To explore the electronic properties of the $P4/nmm$ phase of HBr under pressure, we calculate the electronic band structure, projected density of states (DOS) and Fermi surface. As shown in Fig. 2(a), the existence of large dispersion bands crossing the Fermi level indicates the metallic character. It reveals that states near the Fermi level are mainly composed by the $p$ orbital of bromine atoms. There are three components forming the Fermi surface: a bonelike electron pocket around the $Z$ point, and two nesting hole pockets crossing the $k_z = 0$ plane and composed of orthogonal parallel tubes [presented in Fig. 2(b)]. The Fermi nesting from the parallel Fermi surfaces nearly along the $q_M (0.5, 0.5, 0.0)$ direction can be seen clearly, from both Figs. 2(b) and 2(c). This nesting feature of the Fermi surface resulting from the tetrahedral symmetry could be beneficial to the superconductivity.

FIG. 2: (Color online) (a) Calculated band structures, projected density of states (DOS), and (b) Fermi surface of $P4/nmm$ HBr at 170 GPa. (c) The contour plot of Fermi surface at the plane of $k_z = 0$.

FIG. 3: (Color online) Phonon dispersion curves, Eliashberg spectral functions $\alpha^2 F(\omega)$ together with the electron-phonon integral $\lambda(\omega)$ and phonon density of states (PHDOS) for $P4/nmm$-HBr, $P4/nmm$-HCl$_{0.5}$Br$_{0.5}$ at 170 GPa, and $P4/nmm$-HI at 150 GPa. The phonon linewidth $\gamma_{q,j}(\omega)$ of each mode $(q,j)$ is illustrated by the size of pink circles along the phonon dispersions.
C. Atomic substitution vs. Electron-phonon coupling

As atomic substitution is a common way to induce or enhance superconductivity properties of materials in experiments, we try to raise the $T_c$ in this system with replacing bromine atoms by other lighter halogen atoms. In our calculations, the $P4/nnm$ HCl exhibits insulating character, as shown in Fig. 3(d). The stable pressure for $P4/nnm$ HCl is higher than 200GPa, which agrees with the previous study. The $P4/nnm$ HBr is stable in the pressure from 150 to 200 GPa. Therefore, a possible way to raise $T_c$ is to introduce half substitution of bromine by chlorine atoms. The symmetry of the resulted HCl$_{0.5}$Br$_{0.5}$ compound then becomes to $P4mm$. To illustrate the thermodynamical stability of the $P4mm$ HCl$_{0.5}$Br$_{0.5}$ compound, we calculate its forming enthalpy relative to H$_2$+Cl$_2$+Br$_2$, using the stable phase $C2/c$ of the solid H$_2$ [23] phase $Immm$ of the solid Cl$_2$ [24] and phase $Cmca$ of solid Br$_2$ [25] at the pressure from 150 to 200 GPa. From Table. II, it can be clearly seen that the $P4mm$ HCl$_{0.5}$Br$_{0.5}$ is fairly stable against decomposition.

We performed EPC calculations for HBr, HI in $P4/nnm$ structure and HCl$_{0.5}$Br$_{0.5}$ in $P4mm$ structure, presented in Fig. 3. Here, the Allen-Dynes modified McMillian equation [22]

$$T_c = \frac{\omega_{\text{cutoff}}}{1.2} \exp \left( -\frac{1.04(1+\lambda)}{(\lambda - \mu^*(1+0.62\lambda))} \right)$$

is used to probe their potential superconductivity. From Fig. 3, the low-frequency vibrations are related to the halogen atoms and the high-frequency modes come from the vibrations of the hydrogen atom. The H-stretching modes in HBr give prominent contribution (about 59%) to the integral EPC constant $\lambda$. From Table. IV the results shows that the integral EPC parameter $\lambda$ changes from 1.43 in HBr to 1.93 in HCl$_{0.5}$Br$_{0.5}$ at 170 GPa. With a common Coulomb screening constant value of $\mu^* = 0.1$, the $T_c$ of HBr is estimated to be around 73K, and the HCl$_{0.5}$Br$_{0.5}$ can reach around 95 K at 170 GPa, while the $T_c$ of $P4/nnm$ HI is only about 47 K at 150 GPa.

To get more insights on the reason why the half substitution on HBr can increase $T_c$, the electronic structures of halogen hydrides are calculated in Fig. 4. We can see that the DOS near the Fermi level in HCl$_{0.5}$Br$_{0.5}$ increases compared to that in the HBr and HI compounds and the Van Hove singularity in HCl$_{0.5}$Br$_{0.5}$ is closer to the Fermi level, which is mainly resulting from the halogen atoms. This increase of DOS near the Fermi level may enhance the value of $T_c$. Meanwhile, we analyze the chemical environment of hydrogen atoms in halogen hydrides by calculating the bond length and Bader charges, which are summarized in Table. I. The chlorine, bromine, and iodine atoms have the same number of valence electrons, and the chlorine atom has the strongest electronegativity and least radius among them. It is clear that the length of H-I bond is longer than the H-Br bond in the $P4/nnm$. However, in the $P4/nnm$ structure of HCl$_{0.5}$Br$_{0.5}$, it is abnormal that the length of H-Cl bond is longer than the H-Br bond. Here, we calculate the ELF of $P4mm$ structure for HCl$_{0.5}$Br$_{0.5}$ at 170 GPa (shown in Fig. 5), to explain it. From the Bader charge analysis, the bromine atom changes from the anion to the cation because of the strong electronegativity of substitution of the chlorine atom. So the electrons prefer to locate between the hydrogen and bromine atoms and repel the chlorine atoms, which causes the abnormal elongation of the H-Cl bond and the shortening of the H-Br bond.

The mid-lying optic phonon bands in HCl$_{0.5}$Br$_{0.5}$ are somehow softened due to the unexpected weak H-Cl bond in $P4mm$ HCl$_{0.5}$Br$_{0.5}$. The shorter H-Br bonds make the highest phonon frequency harder compared with that in $P4/nnm$ HBr. Meanwhile, we can see that the gap between the low and high frequencies becomes smaller with the substitution. The increase of intermediated phonon linewidth will enhance the overall electron-phonon coupling constant.
FIG. 5: (Color online) Contour plots of electron localization function (ELF) on the (100) plane along the (a) H-Br and (b) H-Cl bonds, respectively, in the $P_{4}^{4}mm$ HCl$_{0.5}$Br$_{0.5}$ at 170 GPa. (c) Crystal structure of $P_{4}^{4}mm$ HCl$_{0.5}$Br$_{0.5}$. The red, green, and blue balls represent the hydrogen, chlorine, and bromine atoms, respectively.

We note that the low-energy modes at M point goes softening; for both HBr and HCl$_{0.5}$Br$_{0.5}$, the large phonon linewidth of these modes indicates that they are strongly coupled to the electrons. In these modes (see Fig. 5), the vibrations of halogen atoms are in the $ab$ plane with similar strength both in HBr and HCl$_{0.5}$Br$_{0.5}$, while the vibrations of hydrogen atoms are perpendicular to the $ab$ plane. The hydrogen vibrations in HCl$_{0.5}$Br$_{0.5}$ are much stronger than that in HBr, which makes the Br-H-Br and Cl-H-Cl bending amplitude much larger than that of the Br-H-Br bending in HBr. Large amplitude collective motions are usually in low frequency. Although they might be renormalized by anharmonicity for the low frequency, it seems that they do not have a large contribution to the integral EPC constant $\lambda$ as one can see from Fig. 3.

D. $T_c$ and symmetric environment for hydrogen

It was reported earlier that the $T_c$ of $C2/m$ HBr is around $9.7 \times 10^{-3}$ K at 120 GPa\cite{54}, and HBr in the $P4/nmm$ structure exhibits a much superior superconducting transition temperature (about 73 K at 170 GPa). The dramatic difference in superconducting $T_c$ between these two phases indicates that the environment around hydrogen atoms plays a significant role in superconductivity. As we mentioned above, each hydrogen atom in the $P4/nmm$ structure has four tetrahedrally arranged H-Br bonds. This symmetrical environment around hydrogen atoms would harden the H-stretching modes by holding back the vibration of hydrogen atoms. Meanwhile, the average H-Br distance changes from 1.87 Å in $C2/m$ to 1.79 Å in $P4/nmm$ at 150 GPa. The mean absolute percentage deviation of bond length in the $P4/nmm$ structure is 0 but in the $C2/m$ structure is 10.5%. Therefore, we believe that the factors such as a higher coordination number, shorter bond length and a more symmetrical environment of the hydrogen atoms, should be useful to obtain a high $T_c$ superconductor in the H-rich compounds. Actually similar phenomena can also be found in the hydrogen sulfide system\cite{55}.

FIG. 6: (Color online) The vibrational modes at the $M$ point for the lowest twofold degenerate frequency of (a), (b) $P4/nmm$ HBr and (c), (d) $P4/nmm$ HCl$_{0.5}$Br$_{0.5}$. They belong to a 2D $M_3$ irreducible representation.

E. $T_c$ vs. pressure

It is obvious that pressure is an effective method to increase the density of materials, and then to reduce the bond length, get a higher coordination number, and symmetrize the crystal structures. Therefore, high pressure plays a significant role in the research of superconductivity\cite{55,56,57}. We optimize the $T_c$ of halo-
gene hydrides by considering pressure. The main results are summarized in Fig. [7]. The integral EPC constant \( \lambda \) decreases as the pressure rises and the logarithmically averaged phonon \( \omega_{\log} \) has the opposite trend in general. As both of these two parameters have influence on superconducting properties, the resulting \( T_c \) values of halogen hydrides have a complicated evolution with pressure. For HCl\(_{0.5}\)Br\(_{0.5}\) and HBr, \( T_c \) rises and reaches its maximum at around 170 GPa, where it falls down afterwards. However, in the case of HI, \( T_c \) decreases monotonously as the pressure increases. The estimated high values of \( T_c \) for halogen hydrides are summarized in Table. [IV] The \( T_c \) of HCl\(_{0.5}\)Br\(_{0.5}\) in \( P4mm \) structure is found to be as high as 95 K, which is higher than that of all the hydrogen-rich halogen hydrides studied before.

IV. CONCLUSIONS

In this paper, we present a comprehensive analysis of the ground state of HBr at pressures ranging from 150 to 200 GPa based on first-principles calculations. We find that ZPE has a larger effect on the high-symmetry structure than the low symmetry ones. On account of the effect of ZPE, the ground state of HBr should be the 2D netlike \( P4 \) phase, instead of the chainlike \( C2/m \) phase.

Using \textit{ab initio} perturbative linear response calculations, we predict that \( T_c \) of the \( P4/mm \) phase HBr can reach around 73 K at 170 GPa. By substituting half of the bromine atoms in the \( P4/mm \) phase with chlorine atoms, the \( T_c \) of resulted \( P4/mm \) HCl\(_{0.5}\)Br\(_{0.5}\) can reach around 95 K at 170 GPa, which is the highest record among all the known hydrogen halides so far. The \( P4/mm \) and \( C2/m \) phase are closely related to each other with additional bonds and sliding transformation. The energies of these two structures are very close but their estimated superconducting transition temperature is very different, specifically, from 73 K for the \( P4/mm \) HBr to almost non-superconducting for the \( C2/m \) structure. The big difference between them is that the hydrogen atoms in \( P4/mm \) are tetrahedral four-coordinated, while they are two-coordinated in the \( C2/m \) structure, and the HBr bond length in \( P4/mm \) is shorter than that in the \( C2/m \) structure. Our results suggest that in addition to lower atomic mass, larger coordination number, shorter bonds and more restricted symmetrical environment for the light atoms play significant roles in electron-phonon mediated superconductivity. These factors provide guidance in seeking good superconducting materials in the future, which are possibly achievable by pressurization or atomic substitution.

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VI. APPENDIX

| Pressure (GPa) | \( \Delta H \) (meV) |
|---------------|--------------------|
| 150           | -157.26            |
| 170           | -169.44            |
| 200           | -189.06            |

TABLE II: The calculated decomposition enthalpy (defined as \( \Delta H = H_{HCl_{0.5}Br_{0.5}}/2 - H_{H_{2}}/2 - H_{Cl_{2}}/2 - H_{Br_{2}}/2 \) for the \( P4mm \) phase under high pressure, based on the PBE-D2 functional.

| Phase | Pressure (GPa) | \( \lambda \) | \( \omega_{\log} \) (cm\(^{-1}\)) | \( T_c \) (K) |
|-------|---------------|---------------|---------------------------------|--------------|
| \( P4/mm \) | 170           | 1.43          | 665.7                           | 72.5         |
| HBr   | 150           | 0.84          | 726.3                           | 37.6         |
| \( P4/mm \) | 170           | 1.93          | 678.9                           | 95.1         |

TABLE IV: EPC parameter (\( \lambda \)), logarithmic average of phonon frequencies (\( \omega_{\log} \)), and estimated superconducting critical temperature (\( T_c \)) with the Coulomb potential (\( \mu^* \)) of 0.1 for \( P4/mm-HCl_{0.5}Br_{0.5} \), \( P4/mm-HBr \), and \( P4/mm-HI \) under high pressures.
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