

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 95K 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.

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I. INTRODUCTION

In 1935, Wigner and Huntington envisioned that, at low temperature, hydrogen molecular would transform into atomic metallic solid hydrogen under 25 GPa [1]. Later Ashcroft [2] 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 experiments [3–14]. 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 [6] and would reach higher T_c when hydrogen is compressed into denser structures [7]. On the experimental side [3,8–14], 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 so high, it will be difficult to put it into wide applications. Ashcroft [15] 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_4 [15], 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 [16]. 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 [17], CaH_6 with T_c of about 220–235 K at 150 GPa [18], and so on [19–21].

Recently, the sulfur hydrogen system has been identified experimentally to be remarkable high-temperature superconductivity (T_c up to 203 K) under pressure [22]. The measured

T_c of H_3S is consistent with the theoretical results [23] based on Bardeen-Cooper-Schrieffer (BCS) theory [24]. This further strengthens Ashcroft's opinion that the metallization and superconductivity could be realized in hydrogen-dominant compounds [15]. Moreover, the T_c has been predicted to be enhanced by increasing the ionic character in the H_3S compound with a hypothetical alchemical mixture of oxygen [25] and phosphorus [26] atoms, where the T_c of $\text{H}_3\text{S}_{0.925}\text{P}_{0.075}$ in the $Im-3m$ structure at 250 GPa was predicted to be around 280 K [26]. Very recently, as an analog of H_2S , PH_3 was reported to possess a T_c of about 100 K at 200 GPa in experiments [22].

Among the hydrides, the exploration of the superconductivity in halogen hydrides is impelled by the metallization of HCl and HBr [27], where the hydrogen-bond symmetrization plays a critical role [28–31]. The T_c of $Cmcm\text{-H}_2\text{Br}$ and $P6/mmm\text{-H}_4\text{I}$ were theoretically predicted to be around 12.1 K at 240 GPa [32] and 17.5 K at 100 GPa [33], respectively. HCl in $C2/m$ symmetry was calculated to have a T_c of 20 K at 250 GPa [34]. It seems that the T_c values of H-rich halogen hydrides are not very high compared to other hydrides.

In a quantum mechanical system, although the static lattice energy usually contributes the largest part to the total energy, the ZPE can be crucial for determining the stability especially when the energy difference between phases is small. The influence of the ZPE on the energetic stability has been comprehensively tested in the studies of the phase diagram of hydrogen [7,35–37]. Particularly, ZPE tends to be larger in the high symmetric structure, compared to the low symmetric structure [38,39]. In a previous work of HBr system [34], neglecting the effect of ZPE, a $C2/m$ structure is found to be the thermodynamically stable one rather than the $P4/nmm$ structure. However, due to the facts that HBr is a system containing light elements and $P4/nmm$ structure has a higher symmetry than the $C2/m$ structure, we believe that 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 superconducting T_c of the $P4/nmm$ HBr can get a high

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value of 73 K (at 170 GPa). Furthermore, we find that an atomic substituted structure of $\text{HCl}_{0.5}\text{Br}_{0.5}$ 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) [40,41] 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) [42]. Perdew-Burke-Ernzerhof (PBE) [43] and the PBE functional revised for solids (PBEsol) [44] exchange and correlation were employed to investigate the structural stability of HBr, together with Grimmes DFT-D2 method [45] 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 [46] with a k spacing of $0.02 \times 2\pi \text{ \AA}^{-1}$. ZPE was obtained from the quasiharmonic approximation [47,48] from phonon calculations, by finite displacement method implemented in PHONOPY code [49], 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 [50]. 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 [34].

As mentioned above, ZPE is sometimes crucial to judge the stability of structures for compounds with light elements [51]; it has a more notable effect on high-symmetry structures compared with low-symmetry structures. Due to the fact that

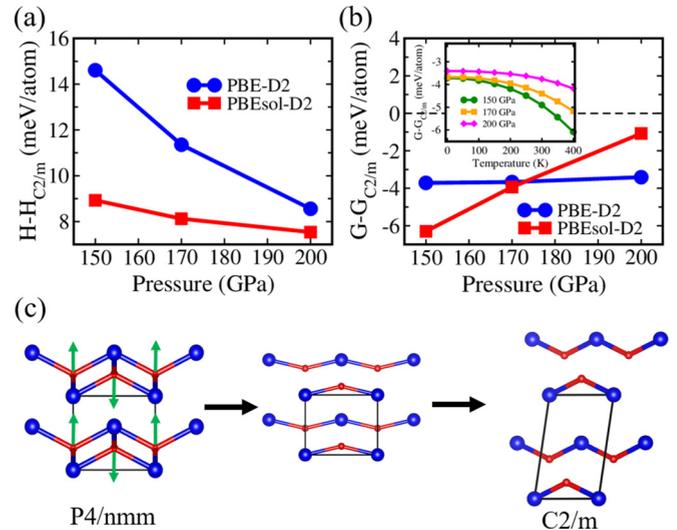


FIG. 1. The calculated enthalpy of $P4/nmm$ HBr relative to the $C2/m$ HBr under pressure, given by the PBE-D2 and PBEsol-D2 functionals, (a) without and (b) with considering the ZPE, respectively. The inset shows the difference of Gibbs free energy of $P4/nmm$ HBr relative to $C2/m$ HBr at different temperature and pressure, 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 chainlike structure.

$C2/m$ 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 [34], 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 chainlike 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 systems [52,53], the DFT-D2 type of vdW correction [45] 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

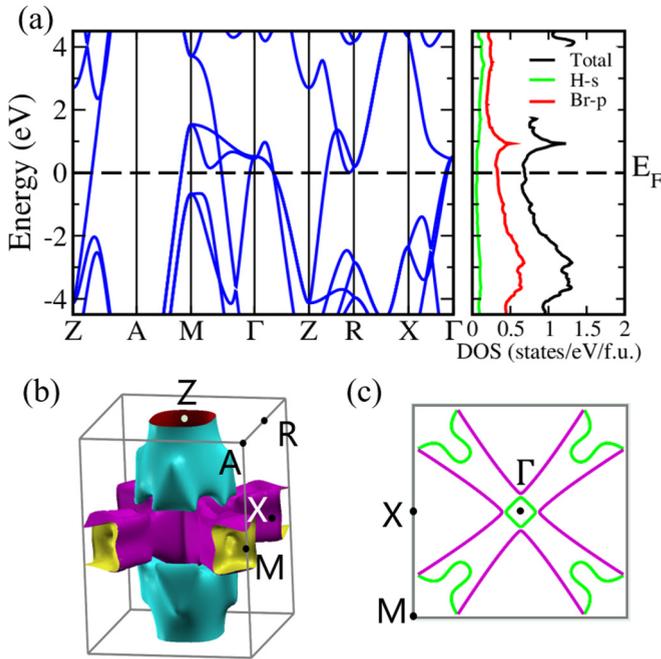


FIG. 2. (a) Calculated band structures, projected density of states (DOS), and (b) Fermi surface of $P4/nmm$ HBr at 170 GPa. (c) The contour plot of Fermi surface at the plane of $k_z = 0$.

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.

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.

C. Atomic substitution vs electron-phonon coupling

As atomic substitution is a common way to induce or enhance superconductivity properties of materials in experiments [54–56], we try to raise the T_c in this system with

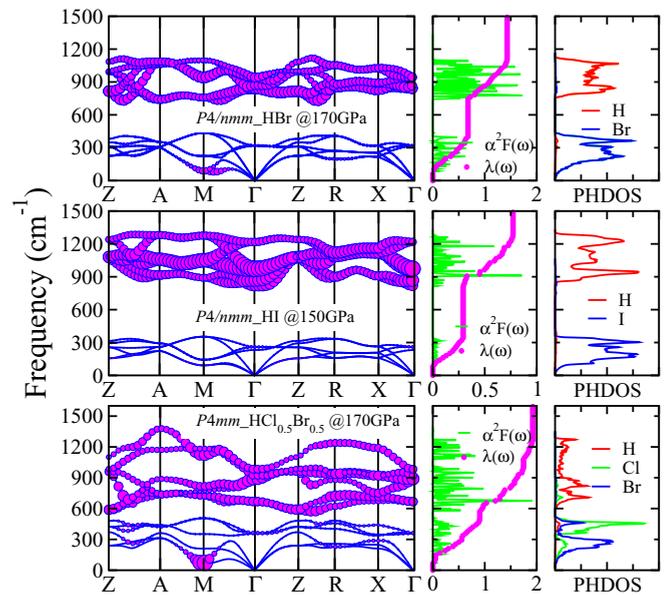


FIG. 3. Phonon dispersion curves, Eliashberg spectral functions $\alpha^2 F(\omega)$ together with the electron-phonon integral $\lambda(\omega)$ and phonon density of states (PHDOS) for $P4/nmm$ -HBr, $P4mm$ -HCl_{0.5}Br_{0.5} at 170 GPa, and $P4/nmm$ -HI at 150 GPa. The phonon linewidth $\gamma_{q,j}(\omega)$ of each mode (q,j) is illustrated by the size of pink circles along the phonon dispersions.

replacing bromine atom by other lighter halogen atoms. In our calculations, the $P4/nmm$ -HF exhibits insulating character, as shown in Fig. 4(d). The stable pressure for $P4/nmm$ HCl is higher than 200 GPa, which agrees with the previous studies [31,34]. The $P4/nmm$ 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 $P4mm$. To illustrate the thermodynamical stability of the $P4mm$ HCl_{0.5}Br_{0.5} compound, we calculate its forming enthalpy relative to $\text{H}_2 + \text{Cl}_2 + \text{Br}_2$, using the stable phase $C2/c$ of the solid H_2 [5], phase $Immm$ of the solid Cl_2 [57], and phase $Cmca$ of solid Br_2 [58] 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 perform EPC calculations for HBr, HI in $P4/nmm$ structure and HCl_{0.5}Br_{0.5} in $P4mm$ structure, presented in Fig. 3. Here, the Allen-Dynes modified McMillian equation [24],

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

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 λ . From Table IV, the results show that the integral EPC parameter λ 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 $\mu^* = 0.1$, the T_c of HBr is estimated to

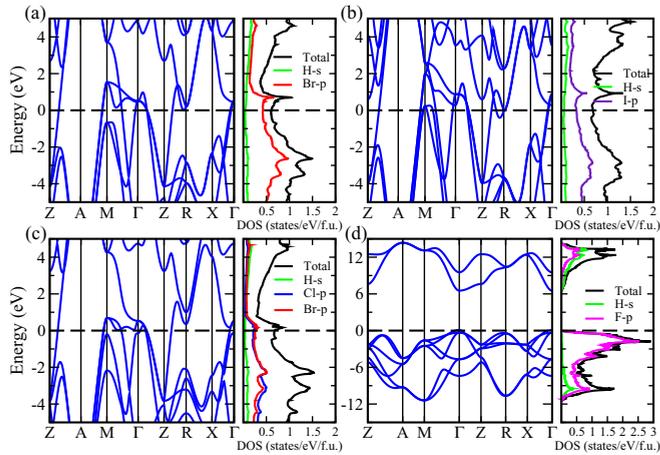


FIG. 4. The calculated band structures and density of states (DOS) for the $P4/nmm$ structure of (a) HBr at 170 GPa, (b) HI at 150 GPa, and (d) HF at 150 GPa. (c) DOS for the $P4mm$ structure of $\text{HCl}_{0.5}\text{Br}_{0.5}$ at 170 GPa.

be around 73 K and $\text{HCl}_{0.5}\text{Br}_{0.5}$ can reach around 95 K at 170 GPa, while the T_c of $P4/nmm$ 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 $\text{HCl}_{0.5}\text{Br}_{0.5}$ increases compared to that in the HBr and HI compounds and the Van Hove singularity in $\text{HCl}_{0.5}\text{Br}_{0.5}$ 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 [26]. 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 $P4/nmm$ structure. However, in the $P4mm$ structure of $\text{HCl}_{0.5}\text{Br}_{0.5}$, 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 $\text{HCl}_{0.5}\text{Br}_{0.5}$ at 170 GPa (shown in Fig. 5) to explain it. From

TABLE I. The calculated Bader charge and bond length of HBr, HI, $\text{HCl}_{0.5}\text{Br}_{0.5}$, and HF. The negative number in Δ charge represents the number of missing electrons.

Compound	Atom	Δ Charge	Bond length (\AA)
$P4/nmm$ HBr (170 GPa)	H	-0.03	H-Br = 1.77
	Br	0.03	
$P4/nmm$ HI (150 GPa)	H	0.23	H-I = 1.93
	I	-0.23	
$P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$ (170 GPa)	H	-0.14	H-Cl = 1.76 H-Br = 1.69
	Cl	0.40	
$P4/nmm$ HF (150 GPa)	H	-0.64	H-F = 1.34
	F	0.64	

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 $\text{HCl}_{0.5}\text{Br}_{0.5}$ are somehow softened due to the unexpected weak H-Cl bond in $P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$. The shorter H-Br bonds make the highest phonon frequency harder compared with that in $P4/nmm$ 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.

We note that the low-energy modes at M point go softening; for both HBr and $\text{HCl}_{0.5}\text{Br}_{0.5}$, the large phonon linewidth of these modes indicates that they are strongly coupled to the electrons. In these modes (see Fig. 6), the vibrations of halogen atoms are in the ab plane with similar strength both in HBr and $\text{HCl}_{0.5}\text{Br}_{0.5}$, while the vibrations of hydrogen atoms are perpendicular to the ab plane. The hydrogen vibrations in $\text{HCl}_{0.5}\text{Br}_{0.5}$ 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 [59]. Although they might be renormalized by anharmonicity for the low frequency,

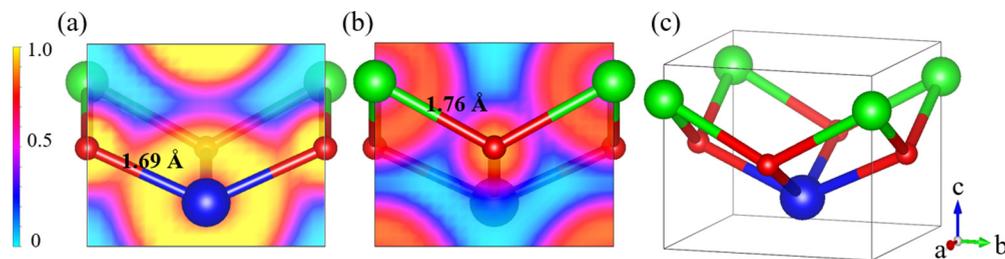


FIG. 5. Contour plots of electron localization function (ELF) on the (100) plane along the (a) H-Br and (b) H-Cl bonds, respectively, in the $P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$ at 170 GPa. (c) Crystal structure of $P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$. The red, green, and blue balls represent the hydrogen, chlorine, and bromine atoms, respectively.

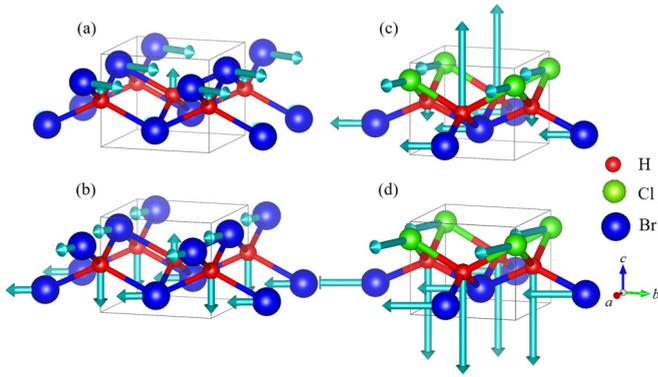


FIG. 6. The vibrational modes at the M point for the lowest twofold degenerate frequency of (a), (b) $P4/nmm$ HBr and (c), (d) $P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$. They belong to a 2D M_3 irreducible representation.

it seems that they do not have a large contribution to the integral EPC constant λ 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 9.7×10^{-3} K at 120 GPa [34], 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 [23].

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 [23,60–62]. We optimize the T_c of halogen hydrides by considering pressure. The main results are summarized in Fig. 7. The integral EPC constant λ decreases as the pressure rises and the logarithmically averaged phonon ω_{\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 $\text{HCl}_{0.5}\text{Br}_{0.5}$ 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

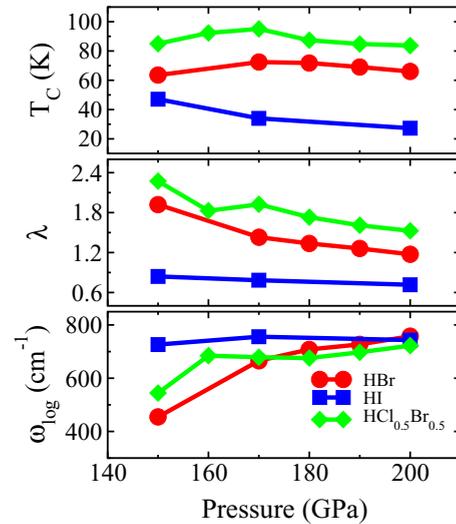


FIG. 7. T_c (red solid line), the integral EPC parameter λ (blue solid line), and the logarithmically averaged phonon frequency ω_{\log} of $P4mm$ - $\text{HCl}_{0.5}\text{Br}_{0.5}$, $P4/nmm$ -HBr, and $P4/nmm$ -HI versus pressure.

monotonously as the pressure increases. The estimated high values of T_c for halogen hydrides are summarized in Table IV. The T_c of $\text{HCl}_{0.5}\text{Br}_{0.5}$ 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 $P4/nmm$ structure, instead of the chainlike $C2/m$ phase.

Using *ab initio* perturbative linear response calculations, we predict that T_c of the $P4/nmm$ phase HBr can reach around 73 K at 170 GPa. By substituting half of the bromine atoms in the $P4/nmm$ phase with chlorine atoms, the T_c of resulting $P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$ can reach around 95 K at 170 GPa, which is the highest record among all the known hydrogen halides so far. The $P4/nmm$ 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 $P4/nmm$ HBr to almost nonsuperconducting for 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.

TABLE II. The calculated decomposition enthalpy (defined as $\Delta H = H_{\text{HCl}_{0.5}\text{Br}_{0.5}} - \frac{1}{2}H_{\text{H}_2} - \frac{1}{4}H_{\text{Cl}_2} - \frac{1}{4}H_{\text{Br}_2}$) for the $P4mm$ phase under high pressure, based on the PBE-D2 functional.

Pressure (GPa)	150	170	200
ΔH (meV)	-157.26	-169.44	-189.06

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APPENDIX

See Tables II–IV.

TABLE III. Detailed structure information of the halogen hydrides at selected pressures.

Phase	Pressure (GPa)	Lattice parameters (Å)	Atomic coordinates (fractional)
$P4/nmm$	170	$a = 3.190$	H(2b) 0.500 0.500 0.500
HBr		$c = 2.636$	Br(2c) 0.500 0.000 0.795
$P4/nmm$	150	$a = 3.488$	H(2b) 0.500 0.500 0.500
HI		$c = 2.823$	I(2c) 0.500 0.000 0.745
$P4mm$	170	$a = 3.074$	H(2c) 0.000 0.500 0.486
$\text{HCl}_{0.5}\text{Br}_{0.5}$		$c = 2.618$	Cl(1a) 0.000 0.000 0.811 Br(1b) 0.500 0.500 0.217

TABLE IV. EPC parameter (λ), logarithmic average of phonon frequencies (ω_{\log}), and estimated superconducting critical temperature (T_c) with the Coulomb potential (μ^*) of 0.1 for $P4mm$ - $\text{HCl}_{0.5}\text{Br}_{0.5}$, $P4/nmm$ -HBr, and $P4/nmm$ -HI under high pressures.

Phase	Pressure (GPa)	λ	ω_{\log} (cm^{-1})	T_c (K)
$P4/nmm$ HBr	170	1.43	665.7	72.5
$P4/nmm$ HI	150	0.84	726.3	37.6
$P4mm$ $\text{HCl}_{0.5}\text{Br}_{0.5}$	170	1.93	678.9	95.1

- [1] E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).
- [2] N. W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).
- [3] H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, *Phys. Rev. Lett.* **63**, 2080 (1989).
- [4] P. Loubeyre, F. Occelli, and R. LeToullec, *Nature (London)* **416**, 613 (2002).
- [5] C. J. Pickard and R. J. Needs, *Nat. Phys.* **3**, 473 (2007).
- [6] P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, and E. K. U. Gross, *Phys. Rev. Lett.* **100**, 257001 (2008).
- [7] J. M. McMahon and D. M. Ceperley, *Phys. Rev. B* **84**, 144515 (2011).
- [8] M. I. Eremets and I. A. Troyan, *Nat. Mater.* **10**, 927 (2011).
- [9] R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharov, and E. Gregoryanz, *Phys. Rev. Lett.* **108**, 125501 (2012).
- [10] I. B. Magdau and G. J. Ackland, *Phys. Rev. B* **87**, 174110 (2013).
- [11] R. S. McWilliams, D. A. Dalton, M. F. Mahmood, and A. F. Goncharov, *Phys. Rev. Lett.* **116**, 255501 (2016).
- [12] P. Dalladay-Simpson, R. T. Howie, and E. Gregoryanz, *Nature (London)* **529**, 63 (2016).
- [13] X. Huang, F. Li, Y. Huang, G. Wu, X. Li, Q. Zhou, B. Liu, and T. Cui, *Chin. Phys. B* **25**, 037401 (2016).
- [14] R. P. Dias and I. F. Silvera, *Science* **355**, 715 (2017).
- [15] N. W. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).
- [16] M. I. Eremets, I. A. Trojan, S. A. Medvedev, J. S. Tse, and Y. Yao, *Science* **319**, 1506 (2008).
- [17] X. Jin, X. Meng, Z. He, Y. Ma, B. Liu, T. Cui, G. Zou, and H. K. Mao, *Proc. Natl. Acad. Sci. USA* **107**, 9969 (2010).
- [18] H. Wang, J. S. Tse, K. Tanaka, T. Iitaka, and Y. Ma, *Proc. Natl. Acad. Sci. USA* **109**, 6463 (2012).
- [19] J. S. Tse, Y. Yao, and K. Tanaka, *Phys. Rev. Lett.* **98**, 117004 (2007).
- [20] G. Gao, A. R. Oganov, A. Bergara, M. Martinez-Canales, T. Cui, T. Iitaka, Y. Ma, and G. Zou, *Phys. Rev. Lett.* **101**, 107002 (2008).
- [21] J. A. Flores-Livas, M. Amsler, T. J. Lenosky, L. Lehtovaara, S. Botti, M. A. L. Marques, and S. Goedecker, *Phys. Rev. Lett.* **108**, 117004 (2012).
- [22] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, *Nature (London)* **525**, 73 (2015).
- [23] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, *Sci. Rep.* **4**, 6968 (2014).
- [24] P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
- [25] C. Heil and L. Boeri, *Phys. Rev. B* **92**, 060508 (2015).
- [26] Y. Ge, F. Zhang, and Y. Yao, *Phys. Rev. B* **93**, 224513 (2016).
- [27] L. Zhang, Y. Wang, X. Zhang, and Y. Ma, *Phys. Rev. B* **82**, 014108 (2010).
- [28] A. Sequeira, H. Rajagopal, and R. Chidambaram, *Acta Crystallogr. Sect. B* **28**, 2514 (1972).
- [29] W. Chen, A. R. H. Walker, S. E. Novick, and F.-M. Tao, *J. Chem. Phys.* **106**, 6240 (1997).
- [30] D. Duan, F. Tian, Z. He, X. Meng, L. Wang, C. Chen, X. Zhao, B. Liu, and T. Cui, *J. Chem. Phys.* **133**, 074509 (2010).
- [31] Q. Zeng, S. Yu, D. Li, A. R. Oganov, and G. Frapper, *Phys. Chem. Chem. Phys.* **19**, 8236 (2017).
- [32] D. Duan, F. Tian, X. Huang, D. Li, H. Yu, Y. Liu, Y. Ma, B. Liu, and T. Cui, *arXiv:1504.01196*.

- [33] A. Shamp and E. Zurek, *J. Phys. Chem. Lett.* **6**, 4067 (2015).
- [34] C. Chen, Y. Xu, X. Sun, and S. Wang, *J. Phys. Chem. C* **119**, 17039 (2015).
- [35] V. V. Natoli, R. M. Martin, and D. M. Ceperley, *Phys. Rev. Lett.* **70**, 1952 (1993).
- [36] S. Azadi, B. Monserrat, W. M. C. Foulkes, and R. J. Needs, *Phys. Rev. Lett.* **112**, 165501 (2014).
- [37] N. D. Drummond, B. Monserrat, J. H. Lloyd-Williams, P. Lopez Rios, C. J. Pickard, and R. J. Needs, *Nat. Commun.* **6**, 7794 (2015).
- [38] D. M. Straus and N. W. Ashcroft, *Phys. Rev. Lett.* **38**, 415 (1977).
- [39] D. M. Ceperley and B. J. Alder, *Phys. Rev. B* **36**, 2092 (1987).
- [40] C. J. Pickard and R. J. Needs, *Phys. Rev. Lett.* **97**, 045504 (2006).
- [41] C. J. Pickard and R. J. Needs, *J. Phys.: Condens. Matter* **23**, 053201 (2011).
- [42] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [43] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [44] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [45] S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- [46] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [47] C. Cazorla and J. Iñiguez, *Phys. Rev. B* **88**, 214430 (2013).
- [48] C. Cazorla and J. Boronat, *Phys. Rev. B* **91**, 024103 (2015).
- [49] A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).
- [50] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [51] I. Errea, M. Calandra, C. J. Pickard, J. R. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, *Nature (London)* **532**, 81 (2016).
- [52] P. Lu, J.-S. Kim, J. Yang, H. Gao, J. Wu, D. Shao, B. Li, D. Zhou, J. Sun, D. Akinwande *et al.*, *Phys. Rev. B* **94**, 224512 (2016).
- [53] K. Xia, J. Sun, C. J. Pickard, D. D. Klug, and R. J. Needs, *Phys. Rev. B* **95**, 144102 (2017).
- [54] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, and L. W. Rupp, *Physica C (Amsterdam)* **165**, 419 (1990).
- [55] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, and S. M. Stishov, *Nature (London)* **428**, 542 (2004).
- [56] S. A. J. Kimber, A. Kreyssig, Y.-Z. Zhang, H. O. Jeschke, R. Valenti, F. Yokaichiya, E. Colombier, J. Yan, T. C. Hansen, T. Chatterji *et al.*, *Nat. Mater.* **8**, 471 (2009).
- [57] P. Li, G. Gao, and Y. Ma, *J. Chem. Phys.* **137**, 064502 (2012).
- [58] B. M. Powell, K. M. Heal, and B. H. Torrie, *Mol. Phys.* **53**, 929 (2006).
- [59] J. Sun, G. Niehues, H. Forbert, D. Decka, G. Schwaab, D. Marx, and M. Havenith, *J. Am. Chem. Soc.* **136**, 5031 (2014).
- [60] L. Gao, Y. Y. Xue, F. Chen, Q. Xiong, R. L. Meng, D. Ramirez, C. W. Chu, J. H. Eggert, and H. K. Mao, *Phys. Rev. B* **50**, 4260 (1994).
- [61] Y. Zhou, J. Wu, W. Ning, N. Li, Y. Du, X. Chen, R. Zhang, Z. Chi, X. Wang, X. Zhu *et al.*, *Proc. Natl. Acad. Sci. USA* **113**, 2904 (2016).
- [62] D. Zhou, Y. Zhou, C. Pu, X. Chen, P. Lu, X. Wang, C. An, Y. Zhou, F. Miao, C.-H. Ho *et al.*, *npj Quantum Mater.* **2**, 19 (2017).