

***Ab initio* study of metallic aluminum hydrides at high pressures**Kazutaka Abe *Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Miyagi 980-8577, Japan*

(Received 30 July 2019; published 13 November 2019)

Metallic phases of Al_2H and AlH at megabar pressures are predicted to be possible by using *ab initio* density functional calculations. The Al_2H phase is stabilized above 155 GPa, where several candidate structures are quite competitive; the structural properties suggest that Al_2H has the phase where Al atoms form an hcp structure and H atoms occupy the octahedral sites in a random manner. The AlH phase is stable above 175 GPa, where the structure takes $R\bar{3}m$ symmetry. Superconducting transition temperature (T_c) of the Al_2H phase is estimated to be of the order of 1 K. In contrast, T_c of the $R\bar{3}m$ AlH reaches 58 K at 180 GPa. The electronic structures around the Fermi energy in the $R\bar{3}m$ AlH are insensitive to pressure compared with those in the well-known $Pm\bar{3}n$ phase of AlH_3 . Accordingly, while theoretical T_c of the $Pm\bar{3}n$ AlH_3 rapidly decreases with compression and becomes almost zero above ~ 200 GPa, that of the $R\bar{3}m$ AlH remains to be 21 K even at 335 GPa. This means that although superconductivity was not observed experimentally in AlH_3 , it might be achieved in AlH .

DOI: [10.1103/PhysRevB.100.174105](https://doi.org/10.1103/PhysRevB.100.174105)**I. INTRODUCTION**

Motivated by the prediction of high-temperature superconductivity of metallic hydrogen by Ashcroft [1], Gilman suggested in 1971 that hydrides in metallic states should also show superconductivity with high transition temperature (T_c) [2]. About three decades later after these theoretical works, again, Ashcroft pointed out the potential of hydrides as high- T_c superconductors, mentioning that the metallization of some hydrides are actually achievable in a diamond anvil cell [3,4]. Indeed, recent experiments are beginning to reveal that hydrides can metallize and become high- T_c superconductors at megabar pressures. In 2015, it was reported by Drozdov *et al.* that sulfur hydride shows superconductivity with T_c of 203 K at 155 GPa [5], where the composition of the sulfur hydride is expected to be SH_3 [6,7]. Also, very recently, lanthanum hydride was found to become a high- T_c superconductor [8]; T_c reaches 260 K at 180 GPa [8] and 250 K at 170 GPa [9]. The composition of this lanthanum hydride is reported to be LaH_{10} [10,11]. In both cases, the compositions of the high- T_c phases are not those usually expected at ambient pressure.

It is interesting to note that AlH_3 was also experimentally metallized at 100 GPa by Goncharenko *et al.* [12], but the metallic phase did not show superconductivity at least up to 164 GPa. The phase has $Pm\bar{3}n$ symmetry as predicted in the preceding work of Pickard and Needs [13]. Curiously, theoretical T_c which was also estimated by Goncharenko *et al.* [12] reaches 24 K at 110 GPa in contradiction to their own experimental findings. To some extent, however, the theoretical results might be considered to be consistent with the experiments. Indeed, the density of states (DOS) at the Fermi energy is not large in the $Pm\bar{3}n$ AlH_3 . The analysis of anharmonicity also indicates that anharmonic effects weaken the electron-phonon coupling [14]. Moreover, the $Pm\bar{3}n$ AlH_3 is predicted to undergo a transition into an insulating phase at higher pressures [15]; this implies that further compression

is not useful in achieving superconductivity in AlH_3 . Yet, it should be stressed that the possibility of aluminum hydrides other than AlH_3 are not fully explored at megabar pressures. According to the aforementioned experimental findings [5,8,9] and recent extensive studies by *ab initio* calculations (see, as review, Refs. [16,17]), it is by no means rare that some unusual compositions are stabilized under compression.

In this paper, main attention being paid to compositions different from AlH_3 , the search for metallic phases of aluminum hydrides is carried out by using *ab initio* calculations. At normal conditions, the possible aluminum hydride AlH_3 has several polymorphic modifications. The most stable of them is α - AlH_3 , whose structure has $R\bar{3}c$ symmetry [18]. Although the $R\bar{3}c$ AlH_3 is still unstable to decomposition into aluminum and hydrogen at one atmosphere, it becomes thermodynamically stable with a little compression. According to Ref. [13], the $R\bar{3}c$ phase is transformed into the $Pnma$ phase at 34 GPa, and then into the $Pm\bar{3}n$ phase at 73 GPa. In experiments at room temperature [12], the $R\bar{3}c$ AlH_3 is transformed into the $P\bar{1}$ phase at 63 GPa, and eventually into the $Pm\bar{3}n$ phase at 100 GPa. In the present study, in addition to the $Pm\bar{3}n$ AlH_3 , other metallic phases of Al_2H and AlH are predicted to be possible above 155 and 175 GPa, respectively. Although T_c of Al_2H is of the order of 1 K at 195 GPa, T_c of AlH is found to be 58 K at 180 GPa. Moreover, AlH is highly metallic and, therefore, the pressure dependence of T_c in AlH is very different from that in AlH_3 which shows a rapid approach to zero above ~ 100 GPa.

II. TECHNICAL DETAILS

Electronic structures are investigated on the basis of the density functional theory (DFT) within the generalized gradient approximation (GGA) [19], where the functional form given by Perdew, Burke, and Ernzerhof [20] is used. The computations are carried out with the use of QUANTUM ESPRESSO [21], where planewave basis sets are employed with ultrasoft

pseudopotentials [22]. The cutoff radii of the pseudopotentials are 1.06 Å for Al, where 3s and 3p electrons are treated as valence electrons, and 0.423 Å for H. The cutoff energy of the planewave basis sets is 816 eV. The k -point number is set greater than $(40 \text{ Å})^3/v_{\text{cell}}$ with v_{cell} being the volume of the simulation cell. For example, the k -point number is taken to be $14 \times 14 \times 14$ for the $Pm\bar{3}n$ AlH_3 at 105 GPa (cubic with $a = 3.125 \text{ Å}$), $14 \times 14 \times 14$ for the $R\bar{3}m$ AlH at 215 GPa (rhombohedral with $a = 5.969 \text{ Å}$ and $\alpha = 23.1^\circ$), and $20 \times 20 \times 10$ for the $P\bar{3}m1$ Al_2H at 195 GPa (hexagonal with $a = 2.360 \text{ Å}$ and $c = 3.830 \text{ Å}$); see Ref. [23] for the candidate structures investigated in this study. A Fermi-Dirac distribution with a temperature of $k_B T = 0.1 \text{ eV}$ is used as a smearing function.

The zero-point energy of nuclei (ZPE) is estimated within the harmonic approximation, where the frozen phonon method is employed with the use of PHONOPY [24]. The number of atoms in each supercell (N_{atom}) is chosen to be 64 or larger for the frozen-phonon calculations. By picking out several candidate structures, it is checked that the choice of $N_{\text{atom}} \sim 64$ almost always makes the finite-size effect on ZPE smaller than $\sim 1 \text{ meV}$ per atom. For example, in AlH_7 with $P\bar{1}$ symmetry at 215 GPa (one of the most hydrogen-rich phases studied here), the ZPE per atom is 263.0 meV with $N_{\text{atom}} = 64$ while that is 262.6 meV with $N_{\text{atom}} = 192$; namely, the difference is just 0.4 meV. One exception where the finite-size error with $N_{\text{atom}} \sim 64$ exceeds 1 meV per atom is the $Pm\bar{3}n$ AlH_3 . The ZPE per atom in the $Pm\bar{3}n$ AlH_3 at 105 GPa is 223.3 meV with $N_{\text{atom}} = 64$, and 225.3 meV with $N_{\text{atom}} = 216$: The ZPE with $N_{\text{atom}} = 64$ (the $2 \times 2 \times 2$ supercell) is 2 meV lower. This is because the use of the $2 \times 2 \times 2$ supercell in the $Pm\bar{3}n$ AlH_3 overestimates the effects of the phonon modes at the X point when constructing the force constants. Indeed, in the $Pm\bar{3}n$ AlH_3 , some of phonon-dispersion curves show a rapid decrease of the frequency in the vicinity of the X point [14], which is due to the band overlap between the conduction band at the R point and the valence band at the M point [12]. The error of 2 meV per atom is practically acceptable since the energy differences of candidate structures are of the order of 10 meV per atom. However, just in case, N_{atom} is increased to 216 in the $Pm\bar{3}n$ AlH_3 . Also, N_{atom} is set to 216 in the $R\bar{3}m$ AlH , where smaller values of N_{atom} lead to quite anisotropic shapes of supercells.

Electron-phonon coupling is investigated by using the density functional perturbation theory [25]. In the calculations of electron-phonon coupling, the number of k points is set larger than $(50 \text{ Å})^3/v_{\text{cell}}$, and that of q points (phonon wave vectors) larger than $(13 \text{ Å})^3/v_{\text{cell}}$. Yet, the numbers are further increased in several cases where the superconducting properties are quite sensitive to the k -point and q -point samplings. For example, in the $Pm\bar{3}n$ AlH_3 , the k -point (q -point) number is taken to be greater than $(65 \text{ Å})^3/v_{\text{cell}}$ [$(20 \text{ Å})^3/v_{\text{cell}}$].

Stable structures are investigated by random structure searches [26–28]. The details of the search method used here are similar to those explained in Refs. [27,28]. The process of the random generation of an initial structure and its constant-pressure optimization is simply repeated until the structure of the lowest enthalpy is encountered at least a few times. Although the minimum number of generated structures is set at 300, the required number of generated

structures reached ~ 3500 in the most difficult case. Throughout the random searches, the k -point number is decreased to about $(20 \text{ Å})^3/v_{\text{cell}}$. After the random searches are finished, a few low-enthalpy structures (with different radial distribution functions) are picked out at each target composition and at each target pressure. Then, refined enthalpy calculations are carried out for those selected structures over a wide range of pressure.

III. STABLE COMPOSITIONS AND STRUCTURAL PROPERTIES

The compositions considered in this study are Al_2H , AlH , AlH_2 , AlH_3 , AlH_4 , AlH_5 , AlH_6 , and AlH_7 . For each composition, random structure searches are performed at 200, 300, and 400 GPa. Simulation cells containing up to four formula units are used; only for Al_2H , AlH , and AlH_2 , simulation cells with six formula units are examined further. The structural parameters of the resulting low-enthalpy structures are summarized in Ref. [23].

The relative enthalpy per atom as a function of the hydrogen concentration is presented in Figs. 1(a), 1(b), 1(c), and 1(d). The lower convex envelopes indicate that the connected compositions are stable. The stability of AlH_3 ($x = 0.75$) is impressive, and no compositions turn out to be possible for $x > 0.75$. For $x < 0.75$, however, Al_2H and AlH are found to be stabilized a little above 150 GPa. While the stabilization pressures of Al_2H and AlH are lowered when ZPE is considered, such an effect of ZPE is not so prominent for $x > 0.75$. This is partly because, for $x > 0.75$, low-enthalpy structures tend to have tight H pairs, whose stretching modes possess rather high frequencies.

The enthalpies of the candidate structures of Al_2H and AlH are compared in Figs. 1(e) and 1(f), respectively. Al_2H is stabilized above 155 GPa, where the phase-separated system consisting of Al and AlH_3 is transformed into the $P\bar{3}m1$ phase. Note, however, that the other four structures (namely, the $R\bar{3}$, $P312$, $P2/m$, and $C2$ structures) also have enthalpies close to that of the $P\bar{3}m1$ structure. This implies that some random nature exists in Al_2H as stated later. In AlH , by contrast, the $R\bar{3}m$ structure is clearly the most stable above 175 GPa; below the pressure, the system undergoes phase separation.

Figure 2 (left) shows the illustration of the $P\bar{3}m1$ Al_2H . In this structure, Al atoms form a slightly distorted hcp lattice, and H atoms occupy the octahedral sites of the hcp-like structure such that they comprise planes perpendicular to the c axis. As mentioned above, the other low-enthalpy structures exist in Al_2H , namely, the $R\bar{3}$, $P312$, $P2/m$, and $C2$ structures in addition to the $P\bar{3}m1$ structure. Actually, all the five structures are quite similar except for the configuration of H atoms. This feature is observed in the radial distribution functions in Fig. 3 (left). The Al-Al radial distribution functions of the five structures agree with each other almost completely up to the second peak [Fig. 3(a)], and the H-Al ones up to the first peak [Fig. 3(b)]. Apparent differences are observed only in the H-H distribution [Fig. 3(c)] since the octahedral sites are occupied by H atoms in different ways. The small enthalpy difference of the five structures hence means that Al_2H is likely to have the phase where H atoms randomly occupy the octahedral sites of the hcp structure of Al atoms.

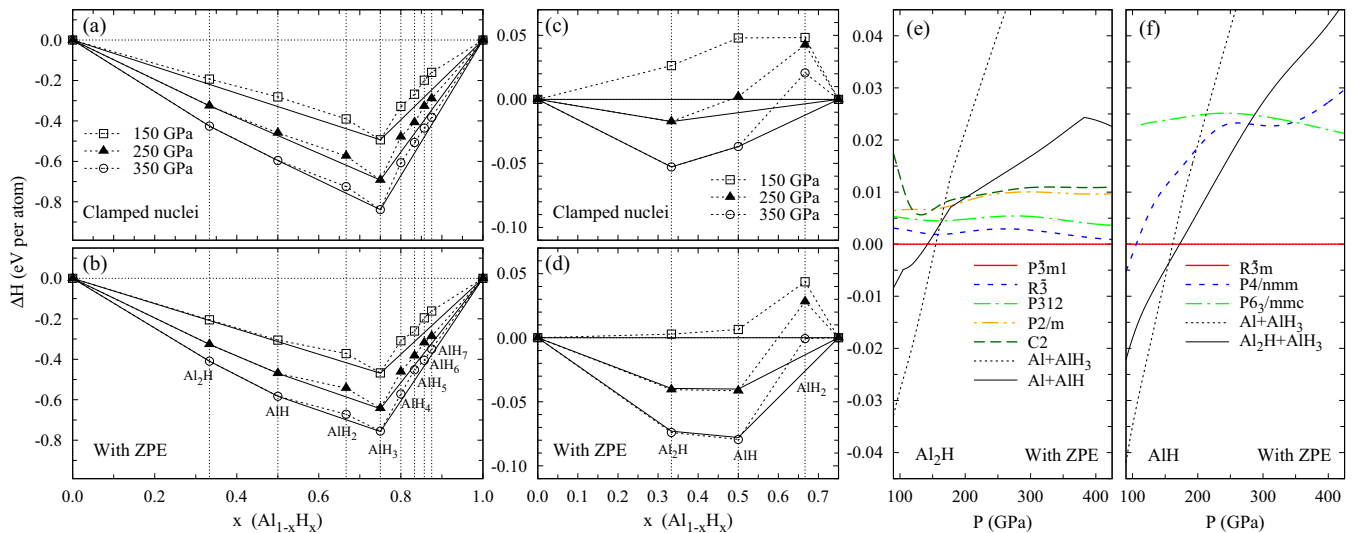


FIG. 1. (a) Relative enthalpy per atom of $\text{Al}_{1-x}\text{H}_x$ as a function of x for $0 \leq x \leq 1$ without ZPE, where stable compositions are connected with solid lines; (b) for $0 \leq x \leq 1$ with ZPE; (c) for $0 \leq x \leq 0.75$ without ZPE; (d) for $0 \leq x \leq 0.75$ with ZPE. (e) Comparison of enthalpy per atom between candidate structures in Al_2H with ZPE; (f) in AlH . The enthalpy of Al is calculated for fcc, hcp, and bcc structures [29–31], and that of H for the C2/c [32], the Cmca-12 [32], the Cmca [33], and the Cs-IV ($I4_1/amd$) [34] structures. Structural parameters of the candidate structures are summarized in Ref. [23].

The structural properties might tempt one to infer further that H atoms can change their positions easily in Al_2H . If this is indeed so, Al_2H is expected to become superionic as temperature is raised, where H atoms are in a liquid state diffusing through the Al solid. As a matter of fact, possibilities of superionic phases have been so far discussed for various hydrides, such as H_2O [36,37], NH_3 [38], and $\text{Ar}(\text{H}_2)_2$ [39]. A rough measure of the robustness of the Al matrix in Al_2H is the melting temperature of pure aluminum, which exceeds 3500 K at 80 GPa [40,41] and is predicted to reach 5150 K at 150 GPa [42]. This melting temperature is much higher than the superionic-transition temperatures of H_2O , NH_3 , and $\text{Ar}(\text{H}_2)_2$ at corresponding pressures [37–39]. Thus, even if the diffusive motion of H atoms makes the melting temperature of the Al matrix lower than that of pure aluminum [39], the attainment of a superionic state seems to be possible.

Now, note that pure aluminum takes the hcp structure above ~ 217 GPa according to experiments at room

temperature [31] (and above ~ 180 GPa in the present calculations). The five low-enthalpy structures proposed for Al_2H , therefore, suggest that the hcp aluminum at high pressures can absorb hydrogen in its octahedral sites. It is then curious to think of an AlH phase which is constructed simply by placing H atoms on all the octahedral sites of the hcp aluminum. However, the resulting AlH phase, whose symmetry is $P6_3/mmc$, has somewhat higher enthalpy than the stable $R\bar{3}m$ phase

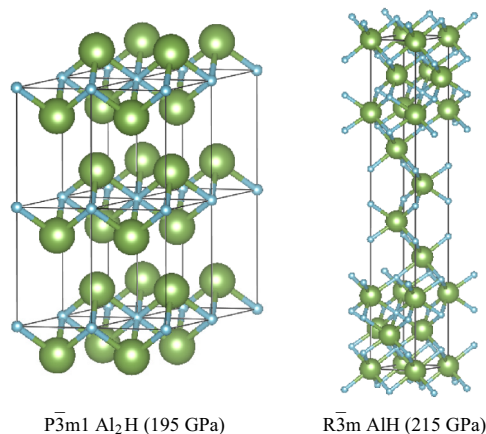


FIG. 2. The lowest-enthalpy structures of Al_2H and AlH [23].

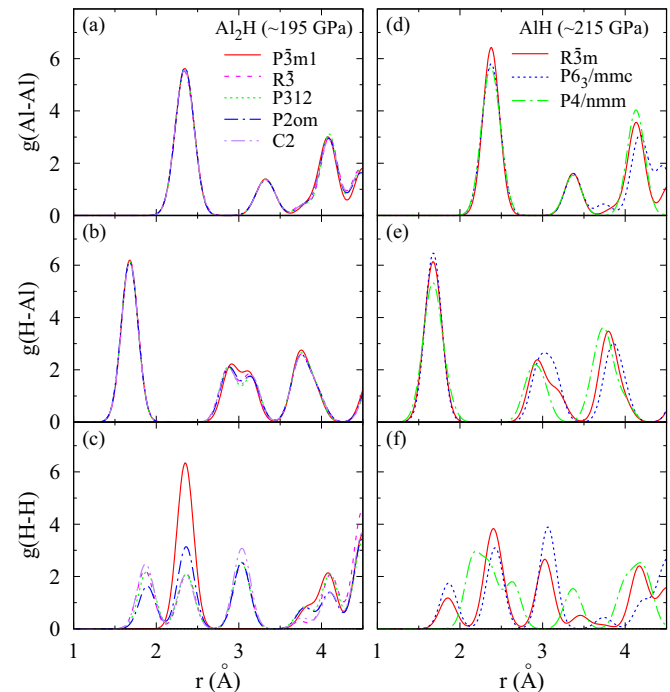


FIG. 3. Radial distribution functions of the candidate structures in Al_2H at $r_s = 1.62$ (left) and AlH at $r_s = 1.57$ (right), where a broadening parameter is set at $0.1 \text{ \AA}$. See Ref. [35] for the definition of r_s .

[Fig. 1(f)]. Thus the hcp $\text{Al}_{1-x}\text{H}_x$ is possible only up to a certain hydrogen concentration x between $1/3$ (Al_2H) and $1/2$ (AlH). The $R\bar{3}m$ structure of AlH is illustrated in Fig. 2 (right). The $R\bar{3}m$ AlH is, in a way, similar to the $P6_3/mmc$ AlH because Al configuration is almost close packed and H atoms occupy the octahedral sites in both phases. Their difference exists in the stacking sequence; the $R\bar{3}m$ AlH is periodic with nine stacking planes. Consequently, there are slight differences even in the Al-Al and the H-Al radial distributions between the $R\bar{3}m$ and $P6_3/mmc$ structures as observed in Fig. 3 (right).

According to Fig. 1(f), the $P4/nmm$ AlH has the lowest enthalpy of the candidate structures below 105 GPa, though it is unstable to decomposition. The $P4/nmm$ AlH has a tetragonally distorted fcc configuration of Al atoms, where H atoms occupy, again, all the octahedral sites. Therefore the radial distribution functions of the $P4/nmm$ AlH are relatively close to those of the $R\bar{3}m$ and $P6_3/mmc$ AlH [Fig. 3 (right)]. It is worth mentioning that the $P4/nmm$ structure of AlH is similar to the structure of the η phase of titanium hydride [43], though their c/a ratios are a little different. The η phase of titanium hydride appears above 7 GPa at room temperature and persists at least up to 30.5 GPa [43]. The composition of the η phase is not clear, but the hydrogen concentration is higher than $\text{TiH}_{0.74}$ (namely, possibly close to TiH). Indeed, recent *ab initio* study proposed the $I4/mmm$ structure of TiH above 25 GPa [44], which is also close to the $P4/nmm$ structure of AlH . In dense hydrides, diagonally adjacent elements on the periodic table sometimes possess similar structures [28]. In this context, it is interesting to note that titanium can be considered to be diagonally adjacent to aluminum [45]. Such a structural similarity is also observed between AlH_3 and GeH_3 [46].

In hydrides of transition-metal and rare-earth elements, there is a tendency that very hydrogen-rich phases are stabilized at high pressures (see, for example, Refs. [47,48]). Contrastingly, the present results show that AlH_3 remains to be the most hydrogen-rich aluminum hydride even at ~ 400 GPa. As a possible cause of this, one might think of the strong ionic nature of aluminum hydrides [15]. However, even for alkali and alkali-earth hydrides (which are likewise highly ionic), very hydrogen-rich phases are proposed [49–51]. Thus it is not so clear at this point why hydrogen-rich aluminum hydrides are unstable. Yet, such a trend is not so unusual, and some other elements close to aluminum on the periodic table also exhibit similar properties. Indeed, stable hydrogen-rich phases have not been found so far regarding beryllium, boron, gallium, carbon, and so on. Also, stable compounds with lower hydrogen concentrations are predicted, for example, for boron (BH) [52], carbon (C_4H_{10}) [53], germanium (GeH_3 , Ge_2H , and Ge_3H) [46,54], and titanium (TiH) [44].

IV. ELECTRONIC AND SUPERCONDUCTING PROPERTIES

A key factor for high- T_c superconductivity in metallic hydrides is partial DOS (PDOS) of H atoms at the Fermi energy. Figure 4 shows that both the $P\bar{3}m1$ Al_2H and the $R\bar{3}m$ AlH have the appreciable PDOS of H atoms at the Fermi energy. Also, both phases have rather delocalized electronic structures. However, a clear difference exists between Al_2H

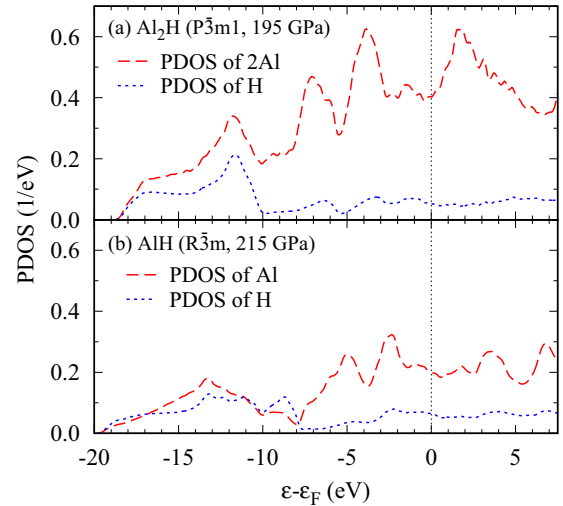


FIG. 4. Partial DOS (PDOS) of the $P\bar{3}m1$ Al_2H at 195 GPa and the $R\bar{3}m$ AlH at 215 GPa.

and AlH : Owing to the difference of their hydrogen concentrations, the contribution of the PDOS of H atoms to the total DOS at the Fermi energy is larger in the $R\bar{3}m$ AlH than in the $P\bar{3}m1$ Al_2H . This indicates that T_c is likely to be higher in AlH than in Al_2H . As expected, this tendency is preserved even when the $R\bar{3}m$ AlH is compared with the $R\bar{3}$, $P312$, $P2/m$, and $C2$ Al_2H .

Table I presents the superconducting properties of Al_2H and AlH together with those of Al and AlH_3 for comparison. The value of T_c is estimated by directly solving the isotropic Eliashberg equation [55]. All the five structures of Al_2H turn out to have relatively low T_c . Nonetheless, the Al_2H phases have much larger electron-phonon coupling parameter λ than the pure hcp aluminum. Hence, doping the hcp aluminum with hydrogen seems to enhance the electron-phonon coupling

TABLE I. Electron-phonon coupling parameter λ , logarithmic average phonon frequency $\omega_{\log}$, and superconducting T_c of Al, Al_2H , AlH , and AlH_3 . The value of T_c is estimated by solving the isotropic Eliashberg equation with $\mu^* = 0.13$ [55]. The asterisk on a space-group name means that the structure is not of the lowest enthalpy. See Ref. [56] for the k -point and q -point numbers used in the analysis of the electron-phonon interaction.

	Phase	P (GPa)	λ	$\omega_{\log}$ (K)	T_c (K)
Al	$P6_3/mmc$	215	0.093	743	—
Al_2H	$P\bar{3}m1$	195	0.393	1164	3.5
	$R\bar{3}^*$	195	0.313	1195	0.6
	$P312^*$	195	0.316	1190	0.6
	$P2/m^*$	195	0.340	1141	1.2
	$C2^*$	195	0.307	1159	0.4
AlH	$R\bar{3}m$	180	0.893	1024	57.9
		215	0.736	1230	45.4
		335	0.534	1555	21.2
AlH_3	$Pm\bar{3}n$	105	0.716	852	28.5
		150	0.471	1000	7.7
		210	0.310	1100	0.3
		290	0.184	1226	—

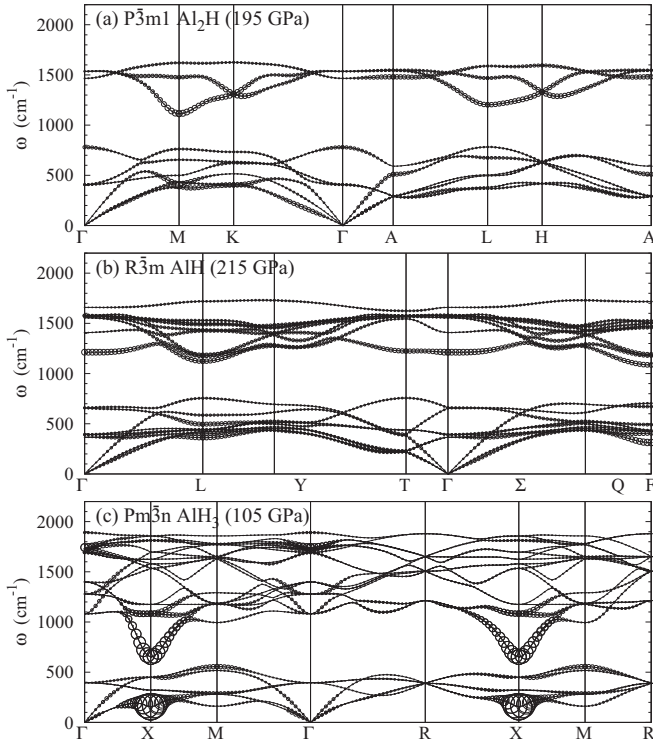


FIG. 5. Phonon dispersion relation, where the areas of the circles on the dispersion curves denote the magnitude of partial electron-phonon coupling parameter $\lambda_v(\mathbf{q})$ [14]: (a) the $P\bar{3}m1$ Al_2H at 195 GPa, (b) the $R\bar{3}m$ AlH at 215 GPa, and (c) the $Pm\bar{3}n$ AlH_3 at 105 GPa.

remarkably. In the $R\bar{3}m$ AlH , T_c is rather high reaching ~ 58 K at 180 GPa and ~ 45 K at 215 GPa; notably, these T_c values are higher than that in the $Pm\bar{3}n$ AlH_3 at 105 GPa.

The parameter λ can be decomposed into the contribution from each phonon mode as follows: $\lambda = \sum_v \int_{\text{BZ}} d\mathbf{q} \lambda_v(\mathbf{q}) / \Omega_{\text{BZ}}$, where the integration is carried out over the first Brillouin zone, Ω_{BZ} is the volume of the first Brillouin zone, and $\lambda_v(\mathbf{q})$ is the partial electron-phonon coupling parameter of the v th phonon mode at wave vector $\mathbf{q}$ [see, for example, Ref. [14] for $\lambda_v(\mathbf{q})$]. In Fig. 5, phonon dispersion relation is shown together with $\lambda_v(\mathbf{q})$ for the $P\bar{3}m1$ Al_2H , $R\bar{3}m$ AlH , and $Pm\bar{3}n$ AlH_3 phases. In the $R\bar{3}m$ AlH [Fig. 5(b)], many modes with various frequencies and wave vectors contribute to λ . Contrastingly, in the $Pm\bar{3}n$ AlH_3 [Fig. 5(c)], major contributions to λ come from the modes around the X point whose frequencies are below $\sim 1000 \text{ cm}^{-1}$ as already pointed out in Refs. [12,14]. Although $\lambda_v(\mathbf{q})$ is remarkably large for those X-point modes, it tends to be very small for the other modes. Accordingly, once $\lambda_v(\mathbf{q})$ is averaged over $\mathbf{q}$, the net value is not so large as expected. Indeed, λ in the $Pm\bar{3}n$ AlH_3 at 105 GPa is 0.716, which is just comparable to λ in the $R\bar{3}m$ AlH at 215 GPa ($\lambda = 0.736$). Furthermore, since the frequencies of those X-point modes are low, $\omega_{\log}$ also becomes low in the $Pm\bar{3}n$ AlH_3 .

At this point, it is interesting to compare the pressure dependence of T_c between the $R\bar{3}m$ AlH and the $Pm\bar{3}n$ AlH_3 . Although T_c is decreased in both phases as pressure is raised, the decrease in the $R\bar{3}m$ AlH is a lot more moderate (Table I).

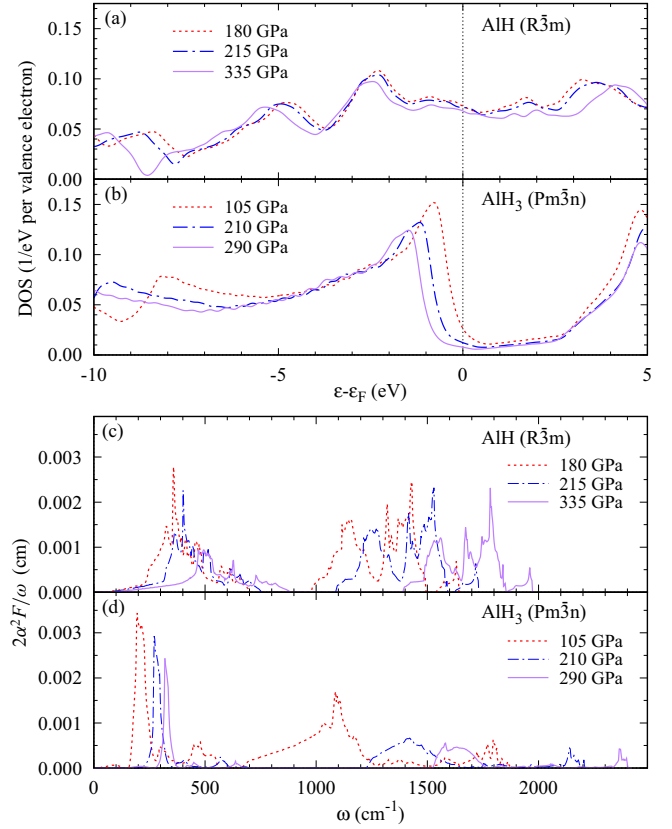


FIG. 6. Pressure dependencies of the DOS (top two panels) and the Eliashberg function α^2F multiplied by $2/\omega$ (bottom two panels) in the $R\bar{3}m$ AlH and the $Pm\bar{3}n$ AlH_3 .

This difference between the two phases can be understood by looking at the pressure dependence of their DOS in Figs. 6(a) and 6(b). While the DOS at the Fermi energy of the $R\bar{3}m$ AlH is quite insensitive to pressure, that of the $Pm\bar{3}n$ AlH_3 is rapidly decreased as pressure is raised. In fact, as predicted by Geshi and Fukazawa [15], the $Pm\bar{3}n$ AlH_3 eventually undergoes the pressure-induced metal-to-insulator transition.

Regarding superconducting properties in the $Pm\bar{3}n$ AlH_3 , it is said that a disagreement exists between experiment and theory [12]: Although superconductivity is not observed experimentally down to 4 K from 120 to 164 GPa in AlH_3 , T_c is theoretically predicted to be high (for example, 24 K at 110 GPa in Ref. [12] and 28.5 K at 105 GPa in Table I). One possible cause is the harmonic approximation. Indeed, Rousseau and Bergara [14] pointed out that in the $Pm\bar{3}n$ AlH_3 , the consideration of anharmonic effects improves the theoretical estimate of T_c . On the other hand, it is also worth paying attention to the prospective metal-to-insulator transition in the $Pm\bar{3}n$ AlH_3 . Geshi and Fukazawa [15] showed that although the pressure of the metal-to-insulator transition is 200 GPa in the GW approximation [57], it is raised up to 300 GPa in the DFT within the GGA. That is to say, the DFT within the GGA overestimates the DOS at the Fermi energy in the $Pm\bar{3}n$ AlH_3 . This overestimate certainly makes the resulting T_c higher, and can be another cause of the disagreement between experiment and theory. Here, it should be stressed that the $R\bar{3}m$ AlH

is almost irrelevant to such a complication in assessing the electronic structures around the Fermi energy because the phase is highly metallic [Fig. 6(a)].

The moderate decrease of T_c upon compression in the $R\bar{3}m$ AlH (Table I) is brought about by the hardening of phonon modes. Figures 6(c) and 6(d) show the Eliashberg function α^2F multiplied by $2/\omega$ in the $R\bar{3}m$ AlH and the $Pm\bar{3}n$ AlH₃, respectively. In the $R\bar{3}m$ AlH, as pressure is raised, α^2F is almost simply shifted to a high frequency region owing to the hardening of phonon modes. This shift weakens $2\alpha^2F/\omega$ (because of the factor $1/\omega$) and, therefore, decreases the electron-phonon coupling parameter $\lambda \equiv \int d\omega 2\alpha^2F/\omega$. Although the shift raises $\omega_{\log}$, the decrease of λ is more significant resulting in the reduction of T_c . In the $Pm\bar{3}n$ AlH₃, on the other hand, α^2F is not only shifted but also weakened owing to the decrease of the DOS at the Fermi energy. Note that in the $Pm\bar{3}n$ AlH₃, low-frequency phonons below 400 cm⁻¹ contribute to λ in a crucial manner as found in Fig. 6(d). In such a case, the changes of phonon frequencies stemming from anharmonicity strongly affect T_c [14]. Low-frequency peaks of $2\alpha^2F/\omega$ are likewise observed in the $R\bar{3}m$ AlH, and the anharmonic effects on T_c should exist to some extent. However, as pressure is raised, the role of the low-frequency modes becomes less significant. Moreover, the low-frequency peaks in the $R\bar{3}m$ AlH consist of the contributions from various modes all over the Brillouin zone as observed in Fig. 5(b); namely, the electron-phonon coupling is not dominated by some specific modes (as in the $Pm\bar{3}n$ AlH₃). This suggests that T_c is not so sensitive to anharmonicity in the $R\bar{3}m$ AlH as in the $Pm\bar{3}n$ AlH₃.

V. SUMMARY

By performing first-principles calculations, dense aluminum hydrides have been investigated at megabar pressures. Although very hydrogen-rich phases are not stabilized, the metallic Al₂H and AlH are possible in addition to the metallic AlH₃ which was already attained in experiments [12]. Several competitive structures are found out for Al₂H above 155 GPa. The structural properties indicate that Al atoms form an hcp structure and H atoms randomly occupy the octahedral sites; this further implies the occurrence of a superionic phase at high temperatures. Every candidate structure of Al₂H has relatively low T_c because of the low hydrogen concentration, though the electron-phonon coupling is much stronger in Al₂H than in pure hcp aluminum. In AlH, the $R\bar{3}m$ structure shows clear stability above 175 GPa. Also, the estimated T_c reaches about 58 K at 180 GPa in the $R\bar{3}m$ AlH.

The value of T_c is higher in the $R\bar{3}m$ AlH than in the $Pm\bar{3}n$ AlH₃. More importantly, T_c of the $R\bar{3}m$ AlH is less sensitive to pressure and remains to be high even above 300 GPa. The moderate pressure dependence of T_c in the $R\bar{3}m$ AlH originates in its highly metallic character; this is a chief difference from the $Pm\bar{3}n$ AlH₃, which becomes nonmetallic above 200 GPa [15]. These findings suggest that the experimental observation of superconductivity is much more expected in AlH than in AlH₃.

ACKNOWLEDGMENT

The author is grateful to Y. Mitsumori for his helpful comments on the manuscript.

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