High-pressure Mg-Sc-H phase diagram and its superconductivity from first-principles calculations

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In this work, global search for crystal structures of ternary Mg-Sc-H hydrides (MgScH6) under high pressure (100 ≤ P ≤ 200 GPa) were performed using the evolutionary algorithm and first-principles calculations. Based on them, we computed the thermodynamic convex hull and pressure-dependent phase diagram of MgScH6 for z/(x + y) < 4. We have identified the stable crystal structures of four thermodynamically stable compounds with the higher hydrogen content, i.e., R5m-MgScH6, C2/m-Mg16ScH16, Immm-MgSc2H7, and Pm3m-Mg(ScH13)6. Their superconducting transition temperatures were computationally predicted by the McMillan-Allen-Dynes formula combined with first-principles phonon calculations. They were found to exhibit superconductivity; among them, R5m-MgScH6 was predicted to have the highest Tc (i.e. 23.34 K) at 200 GPa.

I. INTRODUCTION

Hydrogen-rich hydrides of rare earth metals and alkaline earth metals are now recognized to be viable routes to realize room temperature superconductivity under high pressure. [1–4] These hydrides are usually stabilized with the clathrates consisting of H atoms, which could significantly lower the pressure-volume (PV) term of enthalpy and thus preserve the stability at low pressures. [1, 5–12] In these structures, the H atoms can substantially contribute to the electronic density of states around the Fermi level and also the phonon density of states. Such a feature enables them to be the potential candidates to exhibit high-temperature superconductivity. For instance, theoretical calculations recently have predicted that YH10 with H23 cage structure might exhibit room-temperature superconductivity (286–326 K). [11]

For binary alkaline earth and rare earth hydrides, a systematic search for their crystal structures and superconductivity has been accomplished mostly by theoretical prediction, with the exception of few magnetic rare earth hydrides. [4, 13] The binary hydrides potentially with high-temperature superconductivity have attracted great attention for the experimental verification. LaH10, CaH6, YH6, BaH2, and CeH6 are the examples of the superconducting clathrate structures confirmed in experiments. [8, 14–17] The agreement between the theoretical prediction and the experimental discovery in the superconductivity of these binary hydrides has greatly encouraged the theoretical search for metal hydrides in a more extensive range such as the ternary case.

For ternary cases, a very recent experiment on the La-Y-H system has revealed that the synthesized (La,Y)H10 at P = 180 GPa exhibits a Tc of 253 K. [18] More interestingly, the pressure required for (La,Y)H10 to achieve superconductivity is lower than that of LaH10 high-temperature superconductor, indicating that the ternary hydride has more potential in the search for low-pressure room-temperature superconductivity. [11, 14]

The stability analysis and superconductivity prediction for a minor portion of ternary metal hydrides, such as La-Y-H, Ca-Y-H, Sc-Ca-H, Sc-Y-H, Y-Mg-H, and Ca-Mg-H, have been accomplished recently by theoretical calculations. [18–24] The majority of the high-temperature superconducting compounds in the aforementioned systems prefer to the cage-like structures. For example, Fd3m-CaYH12 with cubic structure, preserves the clathrate structure consisting of the H24 cages, as does CaH6 and YH6. Meanwhile Fd3m-CaYH12 can remain stable above 170 GPa with a Tc value of 254 K as compared to CaH6 and YH6. [1, 5, 20] Theoretical calculations further revealed that the strong electron-phonon coupling (EPC) in these clathrate structures of ternary metal hydrides is associated strongly to the phonon mode of the H-H bond in the cage. [20] Furthermore, the characteristics of these materials look very similar, including the atomic radius, electron number (spd valence electrons), electron negative, atomic mass of constituent elements and so on. [4] This might prevent the H cage from collapsing and preserve the same cage structure and superconductivity in the ternary hydride with clathrate structure. ScCaH6 and ScCaH12 are two potential high-temperature superconductor compounds in the Sc-Ca-H system. The cage structure is preserved in these two compounds and the corresponding Tc values are around 212 K and 182 K at 200 GPa, respectively. [21]

Motivated by the aforementioned studies, herein we concentrated our studies on the Mg-Sc-H system to explore the phase diagram and superconductivity of the associated ternary compounds under high pressure. By employing the evolutionary algorithm for crystal structure prediction, we have found the stable structures of MgScH6, Mg2ScH10, MgSc2H6, and Mg(ScH13)6 under high pressure, which are expected to have the highest hydrogen content in the ternary Mg-Sc-H com-
pounds. In the studied pressure range (i.e., 100-200 GPa), no stable compounds beyond the hydrogen content in the aforementioned compounds were discovered in the hydrogen-rich cases of Mg-Sc-H system, unlike the La-Y-H, Ca-Y-H, and other ternary systems. [18–24] Although some of the stable structures of ternary Mg-Sc-H compounds are predicted to exhibit superconductivity, their superconducting transition temperatures are high up to only 23.34 K at 200 GPa, owing to the relatively low density of states at their Fermi level and also a relatively weak electron-phonon coupling (EPC).

II. METHOD

We considered the fixed compositions of ternary Mg-Sc-H compounds (MgScH$_x$, MgScH$_{x+y}$, MgScH$_{x+1}$, and Mg$_2$ScH$_x$, where $x = 2-12, 14, 16,$ and $18$) along selected lines in ternary convex hull at fixed pressure of 100 and 200 GPa. The crystal-structure search for the Mg-Sc-H systems was performed using the evolutionary algorithm implemented in the USPEX (Universal Structure Predictor: Evolutionary Xtallography) [25] software, together with the first-principles calculations of structural optimization based on density functional theory (DFT).

Our DFT structural optimization was carried out using the VASP (Vienna ab initio simulation package) [26–29] code. The electron-ion interaction is described by the projector augmented wave (PAW) [30, 31] method. The cutoff energy for plane-wave basis sets was set to 600 eV. The exchange and correlation potential was treated by the Perdew-Burke-Ernzerhof (PBE) functional [32] within generalized gradient approximation (GGA).

We computed the ternary convex hull of Mg-Sc-H system using the ConvexHull module in scipy, which involves evaluating Gibbs free energies of the predicted crystal structures at a finite temperature. [33] Their computational details are given in Supplemental Material (SM). The stable ternary phase was determined by a criteria that its enthalpy of formation should be smaller than the whole convex hull plane, which means such a phase would not decompose into any combination of elementary, binary, or other ternary phases.

The EPC and phonons of the stable ternary Mg-Sc-H phases were predicted using the QUANTUM ESPRESSO (QE) suite of programs [34–36] with the PAW method and the Perdew-Burke-Ernzerhof (PBE) [32] exchange correlation functional. The cutoff energy for plane-wave basis sets in the QE calculations was set to 80 Ry. The $k$ (and $q$)-point sampling for Broullion zone integration was set as follows: $4 \times 4 \times 4 \times 4 \times 4 \times 4$ (or $4 \times 4 \times 4$) for MgScH$_x$, $5 \times 5 \times 5 \times 5$ for Mg$_2$ScH$_x$, $3 \times 3 \times 3$ for Mg$_2$ScH$_x$, respectively. The McMillan-Allen-Dynes formula [37] and the Eliashberg function derived from the EPC calculation were used to predict the superconducting critical temperature.

III. RESULTS AND DISCUSSION

A. First-principles phase diagram of Mg-Sc-H system

To determine the ternary phase diagram of Mg-Sc-H system under high pressure, we have taken the Mg-H and Sc-H binary systems [1, 6, 9, 10, 38] as well as the simple substances of constituent elements (Mg, Sc, and H) [39–41] as references in the estimation of thermodynamic stability. It is worth noting that the superconducting structures of the Mg-H and Sc-H binary hydride systems have been discovered recently. For instance, MgH$_6$ and ScH$_7$ have been predicted to exhibit the highest $T_c$ values of around 260 K and 169 K in the Mg-H and Sc-H binary system, respectively. [1, 6, 9, 10, 38] However, the pressure to stabilize these two superconducting compounds are both greater than 300 GPa, which is far beyond the mostly focused high-pressure range (i.e., around 200 GPa) of the widely studied metal hydrides in literature. [1, 5, 20, 42]

To explore the most likely composition for the succeeding experimental synthesis, herein we have sampled a wide phase space of the ternary Mg-Sc-H system at fixed pressures (i.e., 100 GPa and 200 GPa). The ternary phase diagram of the Mg-Sc-H system at 200 GPa is shown in Figure 1, while the results for the pressure at 100 GPa and the associated formation energies are given in the SM. Since most high-pressure studies are carried out under laser heating (1000-2000 K), some metastable phases at 0 K can be stabilized at higher temperatures. [18, 43] Therefore, herein we calculate the ternary phase diagram of Mg-Sc-H system at 200 GPa mainly in three different cases: i) formation enthalpy without considering the zero point energy (ZPE), ii) formation enthalpy with the contribution of ZPE and without the contribution of entropy, and iii) Gibbs free energy with the corresponding entropy contribution at 1000 K.

The stable compounds in the ternary convex hull of Mg-Sc-H system without ZPE at 200 GPa are $Pm\bar{3}m$-Mg$_3$ScH$_3$, $Pm\bar{3}m$-Mg$_3$ScH$_4$, $C2/m$-Mg$_2$ScH$_{10}$, $I4/m$-Mg$_2$ScH$_6$, $P6_3/mmm$-Mg$_2$ScH$_6$, $P6m2$-Mg$_2$ScH$_4$, $R3m$-Mg$_2$ScH$_4$, $I4/m$-Mg$_2$ScH$_5$, $R3m$-Mg$_2$ScH$_5$, $P6_3/mmc$-Mg$_2$ScH$_5$, $R3m$-Mg$_2$ScH$_5$, $R3m$-Mg$_2$ScH$_5$, $P6_3/mmc$-Mg$_2$ScH$_5$, and $R3m$-Mg$_2$ScH$_5$. It is noted that the incorporation of the ZPE contribution leads to the transition of ScH$_4$ from a metastable state to a stable one, which is consistent with the results published by Ye et al. [9] for the binary Sc-H system.

On the other hand, $Pm\bar{3}m$-Mg$_3$ScH$_4$, $P6_3/mmc$-Mg$_2$ScH$_6$, $R3m$-Mg$_2$ScH$_4$, and $R3m$-Mg$_2$ScH$_5$ undergo a change from a stable state to a metastable state because of their large contribution of the ZPE. The four ternary compounds are now equal to the convex hull plane, with energy differences of 0.003, 0.032, 0.008 and 0.015 eV/atom, respectively. Furthermore, we noticed that at a high temperature of 1000 K, $R3m$-Mg$_2$ScH$_5$ can shift from a metastable state to a stable one due to the entropy contribution of lattice vibration. In the binary Mg-H and Sc-H systems, $Cmcm$-MgH$_6$ and $Cmcm$-ScH$_4$ are the stable compounds with the greatest H content in the pressure range of 100-200 GPa. [6, 9] Despite the fact
that most of the existing high-temperature superconducting hydrides are hydrogen-rich compounds, no stable compounds in the extremely hydrogen-rich case have been identified in the pressure range of 100–200 GPa we searched. The ternary diagram package contains the synthetic routes for these stable compounds, and the connections of the binary and unary systems can be used as prospective candidates for the experimental synthesis of the ternary system.

Based on the calculated formation of enthalpy without accounting for the ZPE contribution, we summarize the pressure-dependent phase stability of Mg-Sc-H system and present it in Figure 2. In particular, several phases including $Pm\bar{3}m$-Mg(ScH$_4$)$_3$, $Immm$-MgSc$_2$H$_{10}$, $P6m2$-MgScH$_4$, and $P6_3/mmc$-MgScH$_3$ can be stable in a wide pressure range from 100 GPa to 200 GPa. It is remarkably to note that the Mg-rich ternary Mg-Sc-H phases prefer to be stable in the pressure range toward 200 GPa, while the Sc-rich ones except $R3\bar{m}$-Mg(ScH$_2$)$_2$ can also be stabilized at the pressure of 100 GPa. $P6_3/mmc$-Mg(ScH$_2$)$_2$ can be stable only in the lower pressure range of 100–130 GPa. This trend might be associated with the pressure range of stabilized binary Mg-H and Sc-H hydride systems. At the low pressure, the number of possible stable compounds in the Sc-H system are more than that of the Mg-H system. [6, 9]

### B. Predicted superconductivity of Mg-Sc-H system

Previous studies on the alkali metals and alkaline earth hydrides have shown that the superconducting properties of these hydrides are strongly dependent on the hydrogen content and that the higher $T_c$ is more likely to appear in the hydrogen-rich cases. [1, 4] Herein we pay more attention to $R3\bar{m}$-MgScH$_6$, $C2/m$-Mg$_2$ScH$_{10}$, $Immm$-MgSc$_2$H$_6$, and $Pm\bar{3}m$-Mg(ScH$_4$)$_3$ for their electronic structures and superconductivity because they contain very high hydrogen content.

The crystal structures and the electron localization function (ELF) of these aforementioned four compounds are shown in Figure 3. $R3\bar{m}$-MgScH$_6$ is stable above 150 GPa and has a hexagonal crystal structure, in which each Mg and Sc atom is surrounded by 14 H atoms. The shortest H-H bond length in this structure is about 1.587 Å and the corresponding ELF value at the H-H bond center is about 0.4, indicating a nearly metallic character. The ultra-short distance between atoms translates to a significant ELF value of around 0.7, indicating that the H-H bond in $C2/m$-Mg$_2$ScH$_{10}$ exhibits a strong covalent character. In $Immm$-MgSc$_2$H$_6$ and $Pm\bar{3}m$-Mg(ScH$_4$)$_3$, the shortest H-H bond lengths are 1.628 Å and 1.650 Å, respectively, and the corresponding ELF values at the H-H bond center are 0.3 and 0.1. However the H lattice sites exhibit much greater ELF values. Therefore, the chemical bonding in $Immm$-MgSc$_2$H$_6$ and $Pm\bar{3}m$-Mg(ScH$_4$)$_3$ is mostly ionic interaction. Furthermore, $Pm\bar{3}m$-Mg(ScH$_4$)$_3$ can still form a clathrate structure, in which each Mg and Sc atom is surrounded by the H14 cages. This structure may be regarded as a structure created when the central Sc in $Fm\bar{3}m$-ScH$_3$ is replaced by Mg.

We should point out that $Fm\bar{3}m$-ScH$_3$ does not exhibit superconductivity, as reported previously by Ye et al. [9]. Therefore, the partial substitution of Sc in $Fm\bar{3}m$-ScH$_3$ by Mg triggers the superconductivity in $Pm\bar{3}m$-Mg(ScH$_4$)$_3$.

Figure 4 shows the calculated electronic energy band structure and atom-projected electronic density of states (eDOS) of the aforementioned four structures of great interest. All of them at 200 GPa exhibit metallic feature. Among these four structures, $R3\bar{m}$-MgScH$_6$ has most robust density of states at the Fermi level ($E_F$), while $Pm\bar{3}m$-MgSc$_2$H$_6$ has least density of states at $E_F$. The dominated contributions to the density of states at $E_F$ come from the Sc and H atoms, while the contribution from Mg atoms is negligible. The valence bands in all of these four structures are mainly ascribed to the strong hybridization between Sc and H atoms. At the $E_F$ of $R3\bar{m}$-MgScH$_6$, there are doubly degenerated bands with flat feature along the $Gamma \rightarrow Z$ direction (i.e., parallel to the $c$ axis of the hexagonal unit cell of $R3\bar{m}$-MgScH$_6$). Such a feature of flat band would aid in the electron-phonon interaction. [44] This also lead to the highest $T_c$ of $R3\bar{m}$-MgScH$_6$ among these four structures.

Figure 5 shows the phonon band structure, atom-decomposed phonon density of states (pDOS), and Eliashberg spectra of $R3\bar{m}$-MgScH$_6$, $C2/m$-Mg$_2$ScH$_{10}$, $Immm$-MgSc$_2$H$_6$, and $Pm\bar{3}m$-Mg(ScH$_4$)$_3$ at 200 GPa. At first, we can see that there are no imaginary phonons in all of these four structures and so they are dynamically stable. In addition, their phonons can be clearly grouped into three frequency regions. The low frequency region (i.e., below 20 THz) is dominantly ascribed to the vibration of Mg and Sc atoms because of their heavier atomic masses. The middle frequency region (i.e., centered around 40 THz) and the high frequency region (i.e., above 50 THz) are exclusively contributed by the vibration of H atom.

Table I lists $T_c$ values and their related quantities. The estimated EPC constants ($\lambda$) of these four structures follow the ordering of $R3\bar{m}$-MgScH$_6$ > $C2/m$-Mg$_2$ScH$_{10}$ > $Immm$-MgSc$_2$H$_6$ > $Pm\bar{3}m$-Mg(ScH$_4$)$_3$. Their $T_c$ values exhibit the same ordering. $R3\bar{m}$-MgScH$_6$ is found to have the highest $T_c$ (i.e., 23.3 K) among these four structures at 200 GPa. However, this superconducting temperature is much lower than the reported other metal hydrides with high hydrogen content such as LaH$_{10}$ and YH$_{10}$. [1, 4] This is due to the fact that the contribution of hydrogen atoms to the electronic density of states at $E_F$ of these four structure is too low and the overall EPC constant is also too small. The contribution of heavy atoms (Mg and Sc) to the overall EPC constant in the low frequency range is extremely small, accounting for only about 8%.

It is interesting to note that YH$_3$ and $Fm\bar{3}m$-ScH$_3$ have the same hydrogen content per metal atom with $R3\bar{m}$-MgScH$_6$, $Immm$-MgSc$_2$H$_6$, and $Pm\bar{3}m$-Mg(ScH$_4$)$_3$. However, YH$_3$ has a strong EPC constant of 1.6 and a $T_c$ value of around 40 K. [45] In contrast, the EPC constant of $Fm\bar{3}m$-ScH$_3$ is about 0.23 and it hardly leads to the superconductivity. [9] The EPC
IV. CONCLUSION

In summary, we have employed the evolutionary algorithm in the USPEX code and the first-principles calculations to explore the ternary phase diagram of the Mg-Sc-H system under pressure from 100 to 200 GPa. Our calculations show that the Sc-rich ternary Mg-Sc-H compounds are favorable to be stable around 100 GPa, while the Mg-rich ones are more likely to be stable above 180 GPa. The ternary Mg-Sc-H hydrides with the hydrogen/metal ratio around three have been predicted to exhibit the superconductivity. In particular, the superconducting transition temperature of $R3\bar{m}$-MgScH$_3$ is around 23 K at 200 GPa. Although the superconducting transition temperature of $Pm\bar{3}m$-Mg(ScH$_4$)$_3$ is relatively low, it can be stable in the low range of high pressure toward 100 GPa. Our results provide useful information for the discovery of new low-pressure superconducting hydrides.

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[1] F. Peng, Y. Sun, C. J. Pickard, R. J. Needs, Q. Wu, and Y. Ma, Phys. Rev. Lett. 119, 107001 (2017).
[2] E. Zurek, Comments Inorg. Chem. 37, 78 (2016).
[3] E. Zurek and T. Bi, J. Chem. Phys. 150, 059001 (2019).
[4] D. V. Semenok, I. A. Kruglov, I. A. Savkin, A. G. Kvashnin, and A. R. Oganov, Curr. Opin. Solid State Mater. Sci. 24, 100808 (2020).
[5] H. Wang, J. S. Tse, K. Tanaka, T. Iitaka, and Y. Ma, Proc. Natl. Acad. Sci. 109, 6463 (2012).
[6] X. Feng, J. Zhang, G. Gao, H. Liu, and H. Wang, RSC Adv. 5, 59292 (2015).
[7] J. Hooper, T. Terpstra, A. Shamp, and E. Zurek, J. Phys. Chem. C 118, 6433 (2014).
[8] W. Chen, D. V. Semenok, A. G. Kvashnin, X. Huang, I. A. Kruglov, M. Galasso, H. Song, D. Duan, A. F. Goncharov, V. B. Prakapenka, A. R. Oganov, and T. Cui, Nat. Commun. 12, 1 (2021).
[9] X. Ye, N. Zarifi, E. Zurek, R. Hoffmann, and N. W. Ashcroft, J. Phys. Chem. C 122, 6298 (2018).
[10] S. Qian, X. Sheng, X. Yan, Y. Chen, and B. Song, Phys. Rev. B 96, 094513 (2017).
[11] H. Liu, I. I. Naumov, R. Hoffmann, N. W. Ashcroft, and R. J. Hemley, Proc. Natl. Acad. Sci. USA 114, 6990 (2017).
[12] I. A. Kruglov, D. V. Semenok, H. Song, R. Szczesniak, I. A. Wrorna, R. Akashi, M. M. D. Esfahani, D. Duan, T. Cui, A. G. Kvashnin, and A. R. Oganov, Phys. Rev. B 101, 024508 (2020).
[13] J. A. Flores-Livas, L. Boeri, A. Sanna, G. Profeta, R. Arita, and M. Eremets, Phys. Rep. 856, 1 (2020).
[14] A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Moazzari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, and M. I. Eremets, Nature 569, 528 (2019).
[15] I. A. Troyan, D. V. Semenok, A. G. Kvashnin, A. V. Sadakov, O. A. Sobolevskyi, V. M. Pudalov, A. G. Ivanova, V. B. Prakapenka, E. Greenberg, A. G. Gavriliuk, I. S. Lyubutin, V. V. Struzhkin, A. Bergara, I. Errea, R. Bianco, M. Calandra, F. Mauri, L. Monacelli, R. Akashi, and A. R. Oganov, Adv. Mater. 33, 2006832 (2021).
W. Weckesser, J. Bright, S. J. van der Walt, M. Brett, J. Wilson, K. J. Millman, N. Mayorov, A. R. J. Nelson, E. Jones, R. Kern, E. Larson, C. J. Carey, I. Polat, Y. Feng, E. W. Moore, J. VanderPlas, D. Laxalde, J. Perktold, R. Cimrman, I. Henriksson, E. A. Quintero, C. R. Harris, A. M. Archibald, A. H. Ribeiro, F. Pedregosa, and P. van Mulbregt, Nature Methods 17, 352 (2020).

[34] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).

[35] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncè, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, J. Phys.: Condens. Matter 29, 465901 (2017).

[36] P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. de Gironcoli, P. Delugas, F. F. Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, J. Chem. Phys. 152, 154105 (2020).

[37] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[38] D. C. Lonie, J. Hooper, B. Altintas, and E. Zurek, Phys. Rev. B 87, 054107 (2013).

[39] Q. Liu, C. Fan, and R. Zhang, J. Appl. Phys. 105, 123505 (2009).

[40] Y. Akahama, H. Fujihisa, and H. Kawamura, Phys. Rev. Lett. 94, 195503 (2005).

[41] C. J. Pickard and R. J. Needs, Nat. Phys. 3, 473 (2007).

[42] M. Emaga, M. Sakata, T. Ishikawa, K. Shimizu, M. I. Eremets, A. P. Drozdov, I. A. Troyan, N. Hirao, and Y. Ohishi, Nat. Phys. 12, 835 (2016).

[43] M. Jayaraman, Rev. Sci. Instrum. 57, 1013 (1986).

[44] A. Simon, Angew. Chem., Int. Ed. Engl. 36, 1788 (1997).

[45] D. Y. Kim, R. H. Scheicher, and R. Ahuja, Phys. Rev. Lett. 103, 077002 (2009).

[46] K. Momma and F. Izumi, Journal of Applied Crystallography 44, 1272 (2011).
FIG. 1. Ternary convex hulls of the Mg-Sc-H system at a pressure of 200 GPa. (b), (c) are the convex hulls of Gibbs free energy at finite temperature. The stable and metastable phases are shown by blue circles and red squares, respectively.

FIG. 2. Phase diagram of Mg-Sc-H in the pressure range of 100–200 GPa.

FIG. 3. Predicted crystal structures of (a) $R3m$-MgScH$_6$, (b) $C2/m$-Mg$_2$ScH$_{10}$, (c) $Immm$-MgSc$_2$H$_8$, (d) $Pm3m$-MgSc$_3$H$_{12}$ at 200 GPa. Bottom panels show the corresponding contour plots of electron localization function (ELF) in these structures. These structural models were drawn by using VESTA. [46]
FIG. 4. Electronic band structures and atom-projected electronic density of states of (a) $R\bar{3}m$–MgScH$_6$, (b) $C2/m$–Mg$_2$ScH$_{10}$, (c) Immm–MgSc$_2$H$_9$, (d) $Pm\bar{3}m$–Mg(ScH$_4$)$_3$ at 200 GPa.

FIG. 5. Phonon dispersion and atom-projected phonon density of states (pDOS), and Eliashberg spectral of (a) $R\bar{3}m$-MgScH$_6$, (b) $C2/m$-Mg$_2$ScH$_{10}$, (c) Immm-MgSc$_2$H$_9$, (d) $Pm\bar{3}m$-MgSc$_3$H$_{12}$ at 200 GPa.

TABLE I. $T_c$ estimated by McMillan formula using first-principles phonon calculations for Mg-Sc-H at each pressure. $\lambda$ and $\omega_{\text{pl}}$ are the parameters appearing in the formula.

| Phase     | Space group | $P$ (GPa) | $\lambda$ | $\omega_{\text{pl}}$ (K) | $N_{\text{FB}}$ (states/eVÅ$^3$) at $\mu = 0.1 – 0.13$ | $T_c$ (K) |
|-----------|-------------|-----------|-----------|---------------------------|--------------------------------------------------------|-----------|
| MgScH$_6$ | $R\bar{3}m$ | 200       | 0.536     | 1478.84                  | 0.0150                                                 | 23.34 – 15.08 |
| Mg$_2$ScH$_{10}$ | $C2/m$ | 200       | 0.512     | 1350.17                  | 0.0125                                                 | 17.94 – 11.10 |
| MgSc$_2$H$_9$ | Immm | 200       | 0.410     | 1427.39                  | 0.0120                                                 | 6.88 – 3.14  |
| MgSc$_3$H$_{12}$ | $Pm\bar{3}m$ | 200       | 0.353     | 1377.73                  | 0.0102                                                 | 2.61 – 0.83  |
Supplemental Material

for

First-principles study on the phase diagram and superconductivity of Mg-Sc-H system under high pressure

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A. Computational details

The Gibbs free energy of the chemical compounds in the Sc-Mg-H system was calculated according to the following equation:

\[ G(T) = F(T) + pV, \]  
(S1)

where \( F(T) \) is the Helmholtz free energy as defined below:

\[ F(T) = U(T) - TS(T). \]  
(S2)

The internal energy \( U(T) \) and entropy \( S(T) \) are given by the following equations:

\[ U(T) = E_{\text{elec}} + \int_{0}^{\infty} \left[ \frac{e}{e^{\frac{\varepsilon}{k_B T}} - 1} + \frac{\varepsilon}{2} \right] \sigma(\varepsilon) d\varepsilon, \]  
(S3)

\[ S(T) = \int_{0}^{\infty} \left[ \frac{1}{T e^{\frac{\varepsilon}{k_B T}} - 1} - \frac{k_B \ln(1 - e^{-\frac{\varepsilon}{k_B T}})}{k_B} \right] \sigma(\varepsilon) d\varepsilon. \]  
(S4)

Here \( \sigma(\varepsilon) \) represents the phonon density of states as a function of vibrational energy and is obtained by the lattice dynamics calculation using the Phonopy code.\(^1\) \( E_{\text{elec}} \) is the electronic energy from the DFT calculations.

The superconducting critical temperature was predicted according to the McMillan-Allen-Dynes formula:\(^2\)

\[ T_c = \frac{\omega_{\text{log}}}{1.2 \exp\left( -1.04(1 + \lambda) \right)} \]  
(S5)

where \( \omega_{\text{log}} \) and \( \lambda \) are the logarithmic average phonon frequency and electron-phonon coupling (EPC) constant obtained in the Eliashberg function.
B. Supplementary figures

FIG. S1: Ternary convex hulls of the Mg-Sc-H system at a pressure of 100 GPa.
### C. Supplementary tables

**TABLE S1:** The Gibbs free energy and enthalpy value of Mg-Sc-H at 100GPa at a finite temperature. The metastable phase is shown by the red text in the figure, and the energy value above the convex hull is indicated by the number in brackets.

| Formula   | Space group | Nites | P (GPa) | Enthalpy (eV/atom) | ZPE (eV/atom) | G (T = 0 K) (eV/atom) | G (T = 1000 K) (eV/atom) |
|-----------|-------------|-------|---------|--------------------|---------------|----------------------|--------------------------|
| Mg        | 1m3m        | 1     | 14.0401 | 7.57398           | 0.07276       | 7.64674              | 7.4084                   |
| Sc        | P63/mmc     | 3     | 14.961  | 3.82559           | 0.03295       | 3.85854              | 3.55277                  |
| H         | C2/c        | 12    | 2.8488  | -1.20802          | 0.27219       | -0.93583             | -1.03683                 |
| MgH2      | P63/mmc     | 6     | 5.677   | 0.83324           | 0.21098       | 1.04422              | 0.94367                  |
| MgH4      | Cmcm        | 10    | 4.4777  | -0.02043          | 0.21336       | 0.19293              | 0.1049                  |
| ScH       | Fm3m        | 2     | 8.7637  | 0.17971           | 0.16433       | 0.34405              | 0.14192                  |
| ScH3      | Fm3m        | 4     | 5.5659  | -1.24658          | 0.20921       | -1.03773             | -1.13512                 |
| MgScH2    | P63/mmc     | 10    | 7.0434  | 0.39592           | 0.18754       | 0.58346              | 0.46915                  |
| MgScH4    | P63/mmc     | 6     | 6.1657  | -0.07849          | 0.25699       | 0.1785 (+0.02)       | 0.06299 (+0.01)          |
| MgSc2H4   | I4/mmm      | 6     | 8.3424  | 0.87244           | 0.16994       | 1.04238              | 0.89664 (+0.013)         |
| MgScH3/2  | P63/mmc     | 18    | 6.3831  | -0.33496          | 0.19989       | -0.13507 (+0.002)    | -0.24167 (+0.002)        |
| MgSc2H9   | I4/mmm      | 12    | 5.3076  | -0.77339          | 0.2173        | -0.5561              | -0.64476                 |
| Mg(SbH)3  | Pn3m        | 16    | 5.3679  | -0.90105x         | 0.21949       | -0.68156             | -0.77673                 |

**TABLE S2:** 200GPa

| Formula   | Space group | Nites | P (GPa) | Enthalpy (eV/atom) | ZPE (eV/atom) | G (T = 0 K) (eV/atom) | G (T = 1000 K) (eV/atom) |
|-----------|-------------|-------|---------|--------------------|---------------|----------------------|--------------------------|
| Mg        | 1m3m        | 1     | 11.225  | 13.793            | 0.088         | 13.881               | 13.678                   |
| Sc        | C222        | 3     | 11.385  | 10.272            | 0.042         | 10.314               | 10.062                   |
| H         | C2/c        | 12    | 2.15    | 0.0182            | 0.293         | 0.311                | 0.2417                  |
| MgH2      | P63/mmc     | 6     | 4.598   | 3.372             | 0.267         | 3.639                | 3.562                   |
| MgH4      | Cmcm        | 10    | 3.578   | 1.964             | 0.276         | 2.24                 | 2.173                   |
| ScH       | Fm3m        | 2     | 7.124   | 4.103             | 0.209         | 4.312                | 4.169                   |
| ScH3      | Fm3m        | 4     | 4.654   | 1.282             | 0.258         | 1.540                | 1.457                   |
| ScH4      | F4/mmm      | 5     | 3.956   | 1.022 (+0.007)    | 0.233         | 1.255                | 1.176                   |
| ScH6      | Cmcm        | 14    | 3.462   | 0.711             | 0.263         | 0.974                | 0.907                   |
| Mg3ScH3   | Pn3m        | 7     | 7.149   | 6.464             | 0.205         | 6.669                | 6.543 (+0.02)            |
| Mg3ScH4   | Pn3m        | 6     | 6.384   | 5.415             | 0.196         | 5.611 (+0.015)       | 5.491                   |
| Mg2ScH10  | C2/m        | 13    | 3.999   | 1.888             | 0.261         | 2.149                | 2.074                   |
| MgScH2    | F4/1/amd    | 8     | 6.598   | 4.922             | 0.205         | 5.127                | 5.009                   |
| MgScH3    | P63/mmc     | 10    | 5.722   | 3.551             | 0.289         | 3.84 (+0.032)        | 3.743 (+0.036)           |
| MgScH4    | P6m2        | 6     | 5.069   | 2.7               | 0.229         | 2.928                | 3.743                   |
| MgScH6    | R3m         | 8     | 4.295   | 1.843             | 0.228         | 2.118 (+0.008)       | 2.043 (+0.009)           |
| MgSc2H3   | I4/mmm      | 6     | 6.764   | 4.602             | 0.22          | 4.822                | 4.699                   |
| Mg(SbH)2  | R3m         | 14    | 6.101   | 3.702             | 0.238         | 3.94 (+0.003)        | 3.823                   |
| MgSc2H9   | I4/mmm      | 12    | 4.406   | 1.629             | 0.268         | 1.897                | 1.821                   |
| Mg(SbH)3  | Pn3m        | 16    | 4.464   | 1.532             | 0.266         | 1.799                | 1.722                   |

**TABLE S3:** Crystal structures of Mg-Sc-H predicted at each pressure (P). Lattice parameters (a, b and c) are given in unit of Å.

| Compound   | Space group | P (GPa) | a = b = c (Å) | Atoms | x     | y     | z     |
|------------|-------------|---------|---------------|-------|-------|-------|-------|
| Mg3ScH3    | Pn3m        | 200     | 3.8598        | Mg(3c) | 0.00000 | 0.50000 | 0.50000 |
|            |             |         | a = b = c = 3.8598 | Sc(1a) | 0.00000 | 0.00000 | 0.00000 |
|            |             |         | a = b = c = 3.8598 | H(3d)  | 0.00000 | 0.00000 | 0.00000 |
| Mg3ScH2    | Pn3m        | 200     | 3.44577       | Mg(3d) | 0.00000 | 0.00000 | 0.50000 |
|            |             |         | a = b = c = 3.44577 | Sc(1b) | 0.50000 | 0.50000 | 0.50000 |
|            |             |         | a = b = c = 3.44577 | H(3c)  | 0.00000 | 0.50000 | 0.50000 |

Continued on next page
| Compound     | Space group | $P$ (GPa) | Lattice parameters | Atomic coordinates (fractional) | Atoms  | $x$     | $y$     | $z$     |
|--------------|-------------|-----------|--------------------|---------------------------------|--------|---------|---------|---------|
| Mg$_2$Sc$_{10}$ | $C2/m$      | 200       | a = 4.68347        | Mg(4i) 0.14842 0.50000 0.66872 | Mg(4i) | 0.00000 | 0.00000 | 0.00000 |
|              |             |           | b = 2.66303        | Sc(2a) 0.00000 0.00000 0.00000 | Sc(2a) | 0.00000 | 0.00000 | 0.00000 |
|              |             |           | c = 6.68240        | H(4i) 0.01613 0.00000 0.25389 | H(4i)  | 0.08363 | 0.00000 | 0.50129 |
|              |             |           | $\alpha = \gamma = 90^\circ$ | H(4i) 0.16487 0.50000 0.90258 | H(4i)  | 0.17516 | 0.50000 | 0.15337 |
| MgSc$_2$     | $I4_1/amd$  | 200       | a = b = 3.44323    | Sc(4a) 0.00000 0.00000 0.00000 | Sc(4a) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_3$     | $P6_3/mmc$  | 200       | a = b = 2.68846    | Mg(4b) 0.00000 0.00000 0.00000 | Mg(4b) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_4$     | $P6m2$      | 200       | a = b = 2.81444    | Mg(1a) 0.00000 0.00000 0.00000 | Mg(1a) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_6$     | $R3m$       | 200       | a = b = 2.66735    | Mg(1b) 0.00000 0.00000 0.00000 | Mg(1b) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_4$     | $Immm$      | 200       | a = b = 2.54852    | Mg(1c) 0.33333 0.66667 0.25000 | Mg(1c) | 0.33333 | 0.66667 | 0.25000 |
| MgSc$_6$     | $R3m$       | 300       | a = b = 2.57905    | Mg(1d) 0.00000 0.00000 0.00000 | Mg(1d) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_4$     | $P6_3/mmc$  | 100       | a = b = 2.92493    | Mg(2b) 0.00000 0.00000 0.00000 | Mg(2b) | 0.00000 | 0.00000 | 0.00000 |
| MgSc$_6$     | $Immm$      | 200       | a = b = 2.69052    | Mg(2c) 0.33333 0.66667 0.75000 | Mg(2c) | 0.33333 | 0.66667 | 0.75000 |
| MgSc$_4$H$_{12}$ | $Pm\bar{3}m$ | 200 | a = b = c = 3.85331 | Mg(1b) 0.50000 0.50000 0.50000 | Mg(1b) | 0.50000 | 0.50000 | 0.50000 |
1 A. Togo and I. Tanaka, Scripta Materialia 108, 1 (2015).
2 W. L. McMillan, Phys. Rev. 167, 331 (1968).