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# High-Temperature Superconducting Phase in Clathrate Calcium Hydride $CaH_6$ up to 215 K at a Pressure of 172 GPa

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The recent discovery of superconductive rare earth and actinide superhydrides has ushered in a new era of superconductivity research at high pressures. This distinct type of clathrate metal hydrides was first proposed for alkaline-earth-metal hydride $CaH_6$ that, however, has long eluded experimental synthesis, impeding an understanding of pertinent physics. Here, we report successful synthesis of $CaH_6$ and its measured superconducting critical temperature $T_c$ of 215 K at 172 GPa, which is evidenced by a sharp drop of resistivity to zero and a characteristic decrease of $T_c$ under a magnetic field up to 9 T. An estimate based on the Werthamer-Helfand-Hohenberg model gives a giant zero-temperature upper critical magnetic field of 203 T. These remarkable benchmark superconducting properties place $CaH_6$ among the most outstanding high-$T_c$ superhydrides, marking it as the hitherto only clathrate metal hydride outside the family of rare earth and actinide hydrides. This exceptional case raises great prospects of expanding the extraordinary class of high-$T_c$ superhydrides to a broader variety of compounds that possess more diverse material features and physics characteristics.

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Achieving room-temperature superconductivity is one of the ultimate goals in physics since the discovery of superconductivity in 1911 [1]. While conventional Bardeen-Cooper-Schrieffer (BCS) theory predicts that atomic metallic hydrogen could be the most plausible room-temperature superconductor because of its high Debye temperature and strong electron-phonon coupling [2–5], the realization of solid hydrogen is extremely challenging due to the required high pressures that push the current experimental limits [6–8].

Hydrogen-rich compounds were proposed as alternative candidate materials for exploring high-$T_c$ superconductivity, since the chemical precompression induced by the incorporated elements that hold together hydrogen atoms in the compounds could significantly lower the metallization pressure of hydrogen to experimentally reachable regimes [9,10]. Despite extensive earlier efforts [11–14], the measured or predicted $T_c$ values of compressed hydrides stayed well below those of unconventional cuprate superconductors (up to 164 K at 31 GPa [15]). This situation was changed by the breakthrough discovery in 2012 when an advanced crystal structure search approach predicted a sodalitelike ionic clathrate calcium hydride $CaH_6$ with a remarkably high $T_c$ of 220–235 K at 150 GPa [16]. This Letter was followed by the discovery of superconductivity at 203 K in $H_3S$ under the high pressure of 155 GPa in 2015 [17]. Notably, the high-$T_c$ value of $CaH_6$ is rooted in the clathrate hydrogen framework that closely mimics the physical characteristics and properties of atomic metallic hydrogen, which offers a new design principle and general material platform to search and discover high-$T_c$ hydrogen-rich compounds known as superhydrides [12,13]. Based on the same idea in constructing $CaH_6$, a distinct class of ionic clathrate $MH_6$ hydrides ($M$ represents metal elements) and two new series of rare-earth hydrides $REH_9$ and $REH_{10}$ were later predicted to possess higher $T_c$ values approaching even above room temperature [18,19]. Inspired by these findings, a long list of superconducting superhydrides, including $YH_6$ [20,21], $YH_9$ [21,22], $CeH_9$, $CeH_{10}$ [23], $ThH_9$, $ThH_{10}$ [24], $LaH_{10}$ [25,26], and $(LaY)H_{10}$ [27], were successfully synthesized with observed $T_c$ values ranging from 57 to 262 K at high pressures that agree well with theoretical predictions, opening a new path toward finding room-temperature superconductors.

Conspicuously, all the currently realized high-$T_c$ superhydrides contain rare earth (RE) or actinide (AC) elements as the anchor sites to provide electrons to bind and hold hydrogen atoms into the desired clathrate structure [11–14]. This situation raises fundamental questions about whether this striking capacity can be found among the main-group and transition-metal elements for constructing a larger number and variety of high-$T_c$ superhydrides, which ignites the interest to reexamine the first predicted clathrate superhydride $CaH_6$ [16], which has the lowest stabilization pressure of about 150 GPa among all the non-RE and -AC metal clathrate superhydrides but has stayed out of reach despite repeated experimental attempts.

In this Letter, we report successful synthesis of clathrate $CaH_6$ at pressures of 160–190 GPa and temperature of 2000 K. X-ray diffraction (XRD) and equation of state (EOS) measurements confirm the theoretically predicted crystal structure. Ensuing electrical transport measurements revealed a superconducting transition temperature of 215 K at 172 GPa. These results not only finally verify and confirm the theoretical prediction made almost a decade ago, but, more importantly, offer insights for exploring the hitherto still largely untapped main-group and transition-metal elements to serve as anchor sites in forming superhydrides that may exhibit more diverse structural and superconducting characteristics.

We have prepared 15 cells filled with a mixture of Ca foil and $BH_3NH_3$ as starting materials designated as cell_1 to cell_15. The samples were compressed at room temperature to 160–190 GPa and then heated to about 2000 K with a one-sided pulsed radiation from a yttrium-aluminum-garnet laser. XRD measurements were conducted to determine the crystal structures of the products in cell_1–3. Figure 1(a) shows the XRD patterns of the product in cell_1 at 190 GPa, which do not match any of the known calcium hydrides, such as $CaH_2$, $CaH_4$ [28,29], and $Ca_2H_5$ [28]. Instead, we find that these peaks can be indexed by a body-centered cubic (bcc) lattice of space group $Im\bar{3}m$, with a refined lattice parameter $a = 3.422$ Å ($V = 40.07$ Å$^3$). The volume of this bcc structure agrees well with the previous theoretical prediction of clathrate $CaH_6$ ($V = 40.09$ Å$^3$ at 190 GPa) [16]. Although the occupation details of hydrogen atoms cannot be determined from the experiments due to the weak x-ray scattering cross section, the measured unit cell volumes can be used to estimate the stoichiometry of the hydrides. The bcc unit cell consists of two Ca atoms occupying the atomic volume of 9.41 Å$^3$ per atom [30], leaving 21.25 Å$^3$ for hydrogen atoms. The volume occupied by each hydrogen atom was determined from the extrapolated EOS of $H_2$ to be roughly 1.78 Å$^3$ [31]. On this basis, this experimentally synthesized new calcium hydride can be determined as $CaH_{5.97}$, which has a tiny deviation with the ideal stoichiometry of $CaH_6$.

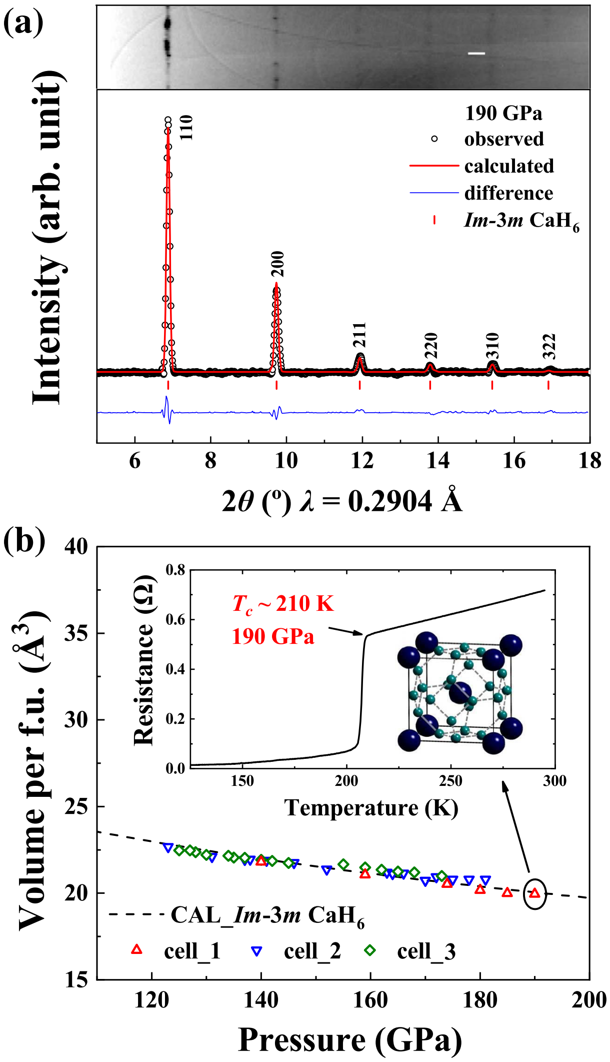

FIG. 1. (a) Synchrotron x-ray diffraction pattern of the clathrate calcium hydride from cell_1 obtained following laser heating of Ca and $BH_3NH_3$ at 190 GPa and the Rietveld refinement of the clathrate $CaH_6$ structure. (b) Experimental EOS from the different samples in this Letter in comparison with that of the predicted clathrate $CaH_6$. The EOS data from cell_1, cell_2, and cell_3 were marked with red triangles, blue inverted triangles, and green rhombus, respectively. The superconducting transition with $T_c \sim 210$ K was observed in the electrical measurement for cell_1 at 190 GPa as shown in the top inset.

Numerical error in this calculation comes from the direct use of elemental phases for the evaluation of atomic volumes. It is as expected that, once a compound is formed, the volumes of constituted elements will somewhat change as compared with their elemental phases. Furthermore, the EOS fitted in the unloading process (Fig. S1 [32]) is highly consistent with the theoretical EOS of $CaH_6$ as shown in Fig. 1(b). All the evidence demonstrates that we have successfully synthesized the long-sought first predicted clathrate superhydride $CaH_6$. It is noteworthy that the diffraction pattern of clathrate $CaH_6$ was also observed in cell_2 and cell_3, as shown in Figs. S2 and S3 [32], with the concurrent appearance of the previously reported $CaH_4$ [28,29].

Previous simulations have indicated that $CaH_6$ would possess an estimated $T_c$ of 220–235 K at 150 GPa [16]. To verify this result, we have conducted electrical transport measurements. Representative electrical resistance measurements as a function of temperature at high pressures are shown in Fig. 2(a), which clearly show superconducting transitions as evidenced by the sharp drop of the resistance at 215, 212, 207, and 212 K at about 172, 170, 181, and 170 GPa, respectively. Among these experiments, zero resistance was observed on samples in cell_4 and cell_5 [inset in Fig. 2(a)], excluding the possibility that the abrupt drop of resistance on cooling arises from structural transitions. To determine the highest value of $T_c$, we evaluated the pressure dependence of $T_c$ as shown in Fig. 2(b). In different experimental runs, $T_c$ fluctuates slightly under the pressure of 170–190 GPa. The highest $T_c$ of 215 K at 172 GPa observed in the sample is consistent with our previous theoretical estimation of 213 K at this pressure (derived from the pressure coefficient of $dT_c/dP = -0.33$ K/GPa) for clathrate $CaH_6$ [16]. Notably, we also conducted electrical measurements on samples in cell_1 and cell_2 before performing XRD measurements and observed a sharp drop of resistance around 210 K as shown in the inset in Figs. 1(b) and S3(a) [32], respectively, indicating that the high-$T_c$ superconductivity indeed comes from clathrate $CaH_6$. Upon decompression, $T_c$ shows a dramatic drop below about 170 GPa as shown in Fig. 2(b). It is interesting to observe that the pressure dependence of $T_c$ varies in different unloading experiments. This may be caused by the different degrees of anisotropic stresses that are present during the decompression process, leading to variable distortions of the crystal lattice in different experiments. It is noted that distortion of the crystal lattice has also been observed in clathrate $LaH_{10}$ [40]. Furthermore, for the sample in cell_7, the decrease of pressure to about 130 GPa leads to the disappearance of superconducting transition as shown in Fig. S5(a) [32], indicating possible decomposition of the superconducting phase. The anomalous resistance peak at about 200 K [the red curve in Fig. 1(a)], which was also observed in $LaH_x$ [26], may be caused by the quantum confinement and coherence effects of inhomogeneous superconductivity in the presence of disorder [41].

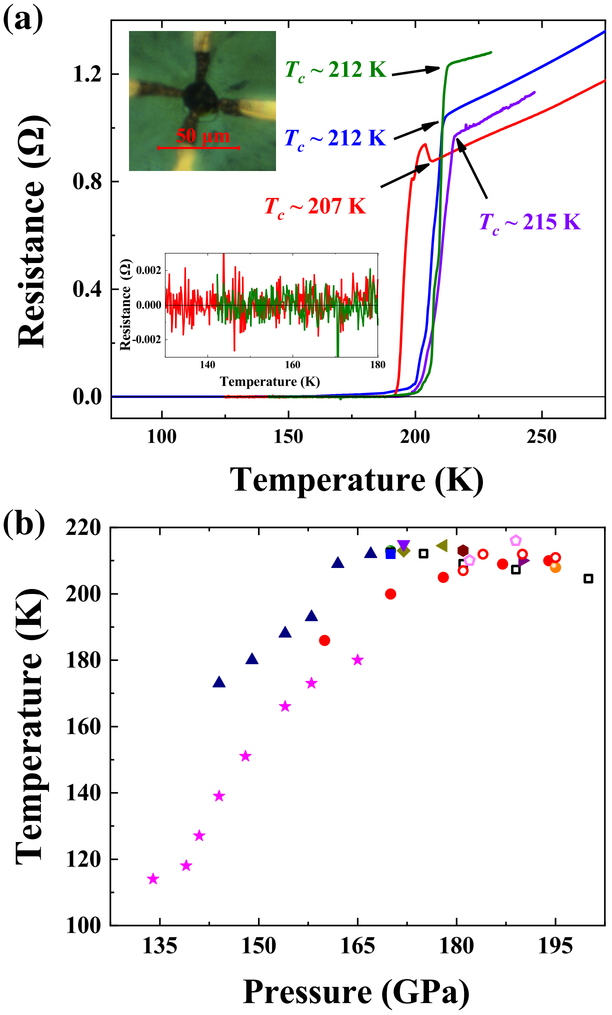

FIG. 2. (a) Resistance measurements on the synthesized clathrate calcium hydride $CaH_6$. Optical micrograph of a sample at 170 GPa after laser heating is shown in the upper left panel inset. Red curve, sample (cell_4) heated at 181 GPa with $T_c \sim 207$ K; olive curve, sample (cell_5) heated at 170 GPa with $T_c \sim 212$ K; blue curve, sample (cell_6) heated at 170 GPa with $T_c \sim 212$ K; purple curve, sample (cell_7) heated at 172 GPa with $T_c \sim 215$ K. The resistance data with near zero values are shown on a smaller scale in the left bottom inset. (b) The dependence of the critical temperature $T_c$ on pressure (cell_1, cell_2, and cell_4–15); the results from 12 different experiments are marked in different colors. The data with the same color are from the same sample in two figures. The open and solid symbols represent the data obtained on compression and decompression, respectively. The temperature dependence of the resistance at high pressures for the symbols of black square (cell_6), navy triangle (cell_8), and magenta star (cell_9) are plotted in Figs. S4, S5(a), and S5(b) [32], respectively.

The typical size of our calcium hydride samples is rather small (20–25 μm in diameter), making it almost impossible to probe the weak signal of magnetic flux expulsion effect in the current experimental capabilities [22,26]. Nevertheless, the superconducting nature of the transitions can be verified by its dependence on external magnetic fields. An applied external field could break the Cooper pairs due to the Pauli paramagnetic effect of electron spin polarization and the diamagnetic effect of the orbital motion, thus reducing the value of $T_c$. As shown in Fig. 3(a), the resistance drop gradually shifts to lower temperatures as the magnetic field is increased in the range 0–9 T at 172 GPa. The upper critical field as a function of temperature, which is defined as 90% of the resistance, is shown in the inset in Fig. 3(b). The application of a

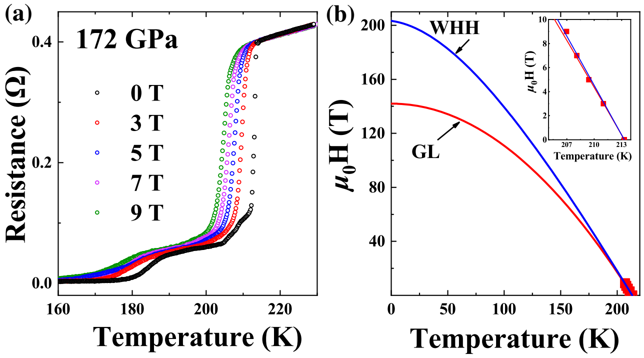

FIG. 3. (a) Temperature dependence of the electrical resistance under applied magnetic fields of $H = 0$, 3, 5, 7, and 9 T at 172 GPa. (b) Upper critical field $H_{c2}$ versus temperature following the criteria of 90% of the resistance in the metallic state at 172 GPa, fitted with the GL and WHH models. Inset: the dependence of the $T_c$ under the applied magnetic field.

magnetic field reduces $T_c$ by about 6 K at $\mu_0 H = 9$ T. The extrapolation values of the upper critical field $\mu_0 H_{c2}(\mathrm{T})$ and the coherence length toward $T = 0$ K are 142 T and 15.2 Å and 203 T and 12.7 Å fitted by the Ginzburg-Landau (GL) [42,43] and Werthamer-Helfand-Hohenberg (WHH) [44] models, respectively. Another independent experiment (cell_11) at 178 GPa (Fig. S6 [32]) shows similar results, producing the $\mu_0 H_{c2}(0)$ and the coherence length estimated with GL and WHH models at 132 T and 15.8 Å and 181 T and 13.5 Å, respectively. The magnitude of the estimated coherence lengths (∼13–16 Å) is well below the typical value (hundreds of angstroms) for type-I superconductors, indicating the $CaH_6$ is a strongly type-II superconductor.

Past studies have attempted to synthesize the predicted high-$T_c$ clathrate calcium superhydride $CaH_6$ but without success [28,29]. One of the probable reasons for the failure of previous experiments is that Ca and pure $H_2$ were used as precursors, whereas Ca easily reacts with $H_2$ at low pressures to form low-hydrogen-content $CaH_x$, such as $CaH_2$, which is hard to further react with $H_2$ [28]. A viable solution is to find hydrogen sources that release $H_2$ only at preferred conditions for $CaH_6$ synthesis. Adopting this idea, $BH_3NH_3$, which releases $H_2$ at higher temperatures, was selected as the hydrogen source in our present Letter, leading to the successful synthesis of clathrate $CaH_6$. After the completion of this Letter, we became aware of another independent experiment by Li *et al.* [45], where similar $T_c$ was also observed in synthesized calcium superhydride using $BH_3NH_3$ as the $H_2$ source.

It should be pointed out that a large number of superhydrides [20–27], including $CaH_6$ in this Letter, have been synthesized under high pressure conditions, some of which, in particular, those clathrate structured superhydrides [20–22,25,26], exhibit extremely high $T_c$ values beyond 200 K. However, recently, Hirsch and Marsiglio [46–50] raised a number of concerns on the interpretation of resistive transitions measured in various superhydrides. Some arguments point to the thermal hysteresis of the resistive transitions [46] and absence of transition broadening under an applied magnetic field [47]. Notably, in our experiment on $CaH_6$, we found that, if the experimental measurements are sophisticatedly performed by eliminating the temperature gradient between the thermal sensor and the samples, the obtained resistance data do not show any thermal hysteresis behavior as shown in Fig. S8 [32]. Moreover, in sharp contrast to some earlier data [26,27,51], we observed in our experiment a clear broadening of the resistive transition under applied magnetic fields (Fig. S9 [32]), which show a similar trend to those of typical standard superconductors, such as $MgB_2$ [52] and NbN [53]. We believe the presented data in Figs. S8 and S9 [32] will make a useful contribution to the field for understanding of debates on the interpretation of resistive transitions in superhydrides.

In summary, we have successfully synthesized the first predicted and long-sought sodalitelike clathrate calcium superhydride $CaH_6$ that exhibits a superconducting transition temperature of 215 K at 172 GPa, which represents the highest $T_c$ value among non-RE ionic superhydrides. This result confirms the original theoretical prediction and provides impetus for further exploration of high-$T_c$ clathrate compounds. The present findings are expected to expand the scope of ongoing studies in search of room-temperature superconductors among more diverse material classes.

This paper is dedicated to the 70th anniversary of the physics of Jilin University.

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