Superconductivity of Lanthanum Superhydride Investigated Using the Standard Four-Probe Configuration under High Pressures

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Recently, the theoretically predicted lanthanum superhydride, $LaH_{10\pm\delta}$, with a clathrate-like structure was successfully synthesized and found to exhibit a record high superconducting transition temperature $T_c \approx 250$ K at ∼170 GPa, opening a new route for room-temperature superconductivity. However, since *in situ* experiments at megabar pressures are very challenging, few groups have reported the ∼250 K superconducting transition in $LaH_{10\pm\delta}$. Here, we establish a simpler sample-loading procedure that allows a relatively large sample size for synthesis and a standard four-probe configuration for resistance measurements. Following this procedure, we successfully synthesized $LaH_{10\pm\delta}$ with dimensions up to $10\times 20\,\mu m^2$ by laser heating a thin La flake and ammonia borane at ∼1700 K in a symmetric diamond anvil cell under the pressure of 165 GPa. The superconducting transition at $T_c \approx 250$ K was confirmed through resistance measurements under various magnetic fields. Our method will facilitate explorations of near-room-temperature superconductors among metal superhydrides.

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Room-temperature superconductivity (RTSC) has been a coveted goal since the discovery of superconductivity in 1911. After almost 110 years of exploration, RTSC remains among the most challenging problems and has attracted enduring enthusiasm among researchers in condensed matter physics and materials science.[1−4] The discovery of cuprate and iron-based high-critical-temperature (T_c) superconductors,[5−7] which are beyond the conventional Bardeen–Cooper–Schrieffer (BCS) theory, was thought to open a possible route toward RTSC. However, the highest attainable T_c (134 K[8]) at ambient pressure (164 K at ∼30 GPa[9]) has remained far below room temperature for almost three decades. In addition, a well-accepted theoretical description of the microscopic mechanism of unconventional superconductivity is still lacking.

Following the seminal work of Ashcroft,[10−12] other researchers have searched for phonon-mediated RTSC in metallic hydrogen or hydrogen-rich materials. According to the BCS theory, high phonon frequencies, large electronic density of states near the Fermi level, and strong electron–phonon coupling benefit high-T_c superconductivity in hydrogen-dominated materials because hydrogen is the lightest element.[10] Although the study on metallic hydrogen has progressed with the development of high-pressure techniques based on the diamond anvil cell (DAC), whether metallic hydrogen is actually formed has not been verified,[13] even under pressures up to ∼400 GPa (the current pressure limit of DACs[14]). However, important breakthroughs in hydrogen-rich materials have been reported in recent years. The discovery of superconductivity with $T_c = 203$ K in H_3S under high pressures[15] provided the first experimental confirmation for the prediction power of the BCS theory for high-T_c superconductivity, reigniting hopes toward achieving RTSC. Accordingly, the stability of crystal structure and the superconducting properties of nearly all binary metal hydrides have been theoretically studies.[1,3,16,18]

Motivated by the theoretical prediction of near-RTSC in rare-earth superhydrides with a clathrate-like structure,[2] two groups have successfully synthe-

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sized lanthanum superhydride, $LaH_{10\pm\delta}$, via direct reaction of La metal with hydrogen or ammonia borane (AB) in DAC upon laser heating at megabar pressures. In 2019, they reported a record high T_c (∼250–260 K) at ∼170–190 GPa.[19,20] The composition stoichiometry of $LaH_{10\pm\delta}$ ($-1 < \delta < 2$) and its crystal structure were determined via synchrotron x-ray diffraction and were confirmed to match well with the theoretical prediction.[2,17,21] Subsequently, many other rare-earth superhydrides have been experimentally explored and high-T_c superconductivity has been discovered in YH_9 ($T_c = 243$ K at 201 GPa[22]) and ThH_{10} ($T_c = 161$ K at 175 GPa[23]).

However, the above-mentioned studies on metastable rare-earth superhydrides were conducted at ultrahigh pressures and required both *in situ* synthesis with laser heating and superconductivity verification by electrical resistance measurements. The experimental procedures are complicated and the tiny samples (typically of dimensions 5–10 µm) are difficult to handle. In this study, we developed a simpler sample-loading procedure that obtains relatively large samples in DAC and successfully synthesizes $LaH_{10\pm\delta}$ with a high T_c (∼ 250 K) at 165 GPa. Our method is suitable for exploring RTSC in metal superhydrides under high pressures.

As already mentioned, the *in situ* synthesis and subsequent resistance measurements of $LaH_{10\pm\delta}$ at megabar pressures are of challenge because of the small culet and sample size in DACs. Our $LaH_{10\pm x}$ was synthesized in a symmetric DAC under pulsed laser heating, and the resistance measurements were performed using the standard four-probe method. The diamond anvils used in this study have a culet of 70 µm and were beveled at ∼8° from a primitive diameter of 300 µm. Sample loading with the proper electrode configuration was crucial for a successful experiment. In previous *in situ* syntheses of $LaH_{10\pm\delta}$, the hydrogen source was pure hydrogen or AB.[19,20] Although pure hydrogen loading increases the hydrogen content (and hence the T_c) of the formed $LaH_{10\pm\delta}$, the hydrogen gas-loading system is complicated and inaccessible to many research groups. In addition, the large shrinkage of the gasket hole caused by the high compressibility of hydrogen can easily damage the electrodes used for resistance measurements. On the contrary, AB is relatively stable under ambient conditions and small amounts of tiny AB crystals are safe to handle. AB decomposes when heated, releasing hydrogen even under megabar pressures. The volume change of compressed AB is smaller than that of loading hydrogen. The effectiveness of AB as the hydrogen source for synthesizing $LaH_{10\pm\delta}$ with T_c over 250 K has been demonstrated in a recent study.[19] Hence, in this study, AB was employed as the hydrogen source.

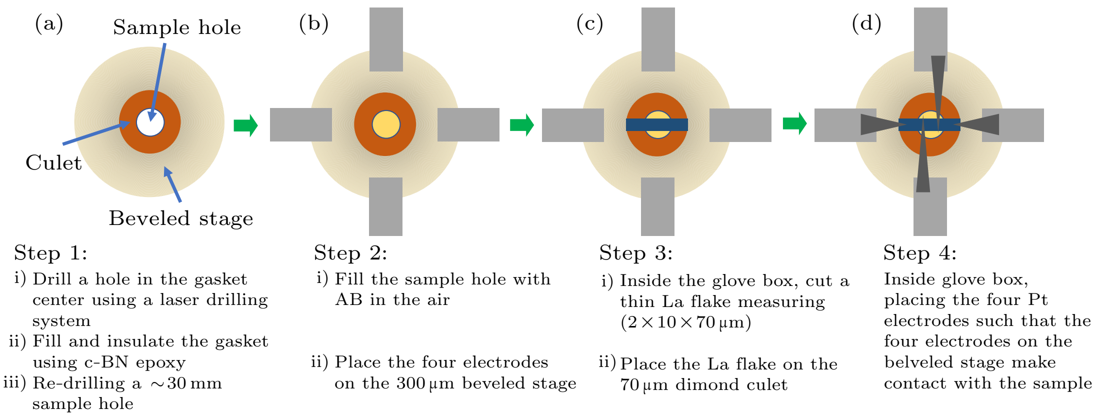

Fig. 1. Scheme for the sample loading of La and AB into the DAC.

For resistance measurements at megabar pressures, the electrodes should be tough and should maintain good contact with the sample. In previous studies on $LaH_{10\pm\delta}$, the electrodes that maintained direct contact with the sample were generally coated on diamond using Pt or Ta in the van der Pauw four-probe configuration.[19,20] The diamond with its electrode coating should be handled carefully to avoid scratching, which can break the contacts. Alternatively, the traditional method, which involves the manual placement of the electrodes on a culet larger than 40–50 µm, can ensure good electrical contact, and this method makes it possible to repair the electrodes in short time. Thus, in this study, we manually placed all the electrodes using the traditional method and loaded one sample in 2–3 days. In addition, we employed the standard four-probe configuration rather than the van der Pauw geometry to avoid changes in the voltage polarity and to improve the data reliability.

Figure 1 shows the sample-loading process incorporated in our study. First, a 250-µm-thick rhenium gasket was pre-indented to ∼30 µm. A 50-µm-diameter hole was then drilled into the gasket using a laser drilling system. The rhenium gasket was covered with a c-BN epoxy insulating layer. Another ∼30-µm hole was drilled in its center and it served as the sample chamber for the AB [see Fig. 1(a)]. Four large electrodes were fixed onto the beveled diamond stage, as shown in Fig. 1(b). In an argon-filled glove box, a thin rectangular La flake with an initial size of approximately $2 \times 10 \times 70\,\mu m^3$ was placed at the center of a 70-µm diamond culet [Fig. 1(c)]. Next, the La flake was connected to the four large electrodes on the beveled stage with four Pt electrical leads in the standard four-probe configuration [Fig. 1(d)]. Here, we should ensure that the voltage leads are in contact with the La inside the sample chamber. Moreover, for a 70-µm diamond culet, the diameter of the sample chamber drilled in the gasket center should be less than 30 µm; otherwise, the AB will flow out of the culet under compression. AB removal from the culet often occurs below 40 GPa; above this pressure, the AB flow is insignificant. Conversely, the sample chamber should not be less than 10 µm in width because the small hydrogen release from AB may not initiate an effective reaction.

After closing the DAC and applying pressure directly to ∼170 GPa, we heated the La + AB in the sample chamber using a continuous 1064-nm YAG laser from the AB side. The laser spot with an approximate diameter of 10 µm was moved forward and backward along the La flake between the two voltage leads, ensuring a sufficient reaction between La and the hydrogen released from AB. The pressure before and after laser heating was determined from the Raman signal of diamond.[24,25] The temperature was determined from the black body irradiation spectra of the sample. After laser heating, the temperature-dependent resistances were measured in a sample-in-vapor He^4 cryostat equipped with a 9 T helium-free superconducting magnet.

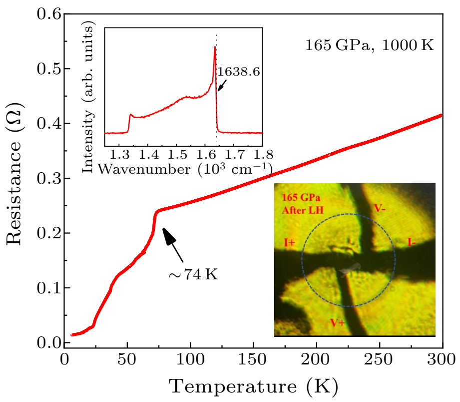

Fig. 2. Temperature dependence of electrical resistance in the first experiment (165 GPa, ∼1000 K). Insets show the diamond Raman signal from which the pressure was determined (top left) and an optical image of the sample in the DAC after laser heating (bottom right).

The main panel of Fig. 2 shows the temperature dependence of electrical resistance for the LaH_x sample synthesized at ∼1000 K and 165 GPa. As seen in the optical image (bottom right), the sample and electrodes in the DAC remained almost intact after laser heating. The resistance of the obtained sample decreased almost linearly as the sample cooled to ∼74 K. At this temperature, the resistance suddenly dropped, followed by a gradual reduction in the resistance with further decrease in the temperature to ∼40 K and 25 K. The superconductive transition at ∼74 K, which is much lower than the reported optimal T_c (∼250 K), can be ascribed to the lower hydrogen content due to the mild heating temperature and/or insufficient AB in the DAC. Similar results in low-H LaH_x were previously reported by Drozdov *et al.*[20]

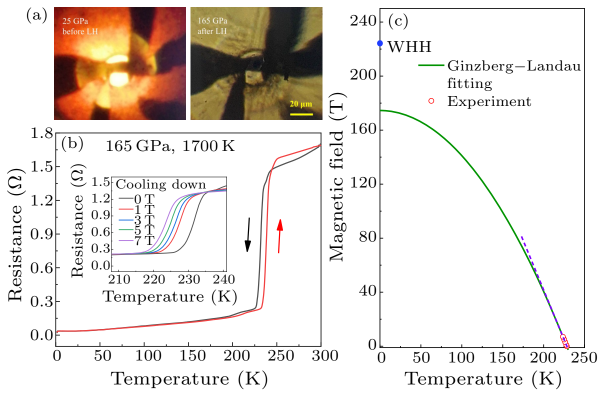

Fig. 3. (a) Optical images of the sample assembly at 25 GPa before laser heating and at 165 GPa after leaser heating; (b) temperature-dependent resistance of $LaH_{10\pm\delta}$ at 0 T over the entire temperature range during the cooling and warming processes (inset shows the resistance near the superconducting transition under different magnetic fields); (c) field dependence of the critical temperature fitted by the Ginzberg–Landau expression (green solid curve). The zero-temperature upper critical field $H_{c2}(0)$ calculated using the Werthamer–Helfand–Hohenberg (WHH) expression in the dirty limit is shown by the blue dot. The violet dashed line represents the linear fitting to obtain the initial slope.

To increase the hydrogen content and facilitate the formation of the clathrate-like structured $LaH_{10\pm\delta}$ with a higher T_c, we performed a second experiment with the highest possible AB loading and increased the temperature of the laser heating to ∼1700 K at 165 GPa. For this synthesis, we reached ∼ 1700 K at a power of 28 W by laser heating the La foil though the diamond anvil and AB layer. We moved the laser along the sample in between the two voltage leads in ten steps and stay for about 1 s at each step. Figure 3(a) presents the optical images taken at 25 GPa before laser heating and at 165 GPa after laser heating. The sample assembly almost retained its original shape after heating, which was crucial for successful synthesis and subsequent resistance measurements. During the cooling and warming processes, the temperature-dependent resistance of the obtained sample began dropping at T_c^{onset} of $\sim$240 K and $\sim$250 K, respectively [Fig. 3(b)], consistent with the superconducting transition reported by Drozdov *et al.*[20] The superconducting transition was relatively sharp but failed to reach zero resistance upon further cooling, presumably due to the contact between the voltage and current probes and/or the presence of an unreacted portion in the sample. Here, because the temperature sensor was attached to the stainless steel frame of diamond anvil cell, the measured temperature is ahead of the actual sample temperature. As a result, the observed superconducting transition exhibits some thermal hysteresis even though we cooled and warmed the sample in a slow rate of $\sim$0.7 K/min.

The superconducting transition was further verified by measuring the temperature-dependent resistance under external magnetic fields. As shown in the inset of Fig. 3(b), the resistance drop gradually shifted to lower temperatures as the magnetic field increased. Here, we defined the superconducting T_c^{mid} as the temperature corresponding to 50% of the resistance drop. Figure 3(c) plots the obtained T_c^{mid} values as a function of external magnetic field up to 7 T. From this plot, the upper critical field $H_{c2}(0)$ was estimated to be 174 T and 223 T according to the Ginzberg–Landau and the Werthamer–Helfand–Hohenberg expressions,[26] respectively. The obtained $H_{c2}(0)$ values are greater than those reported by Drozdov *et al.*,[20] presumably due to the quite narrow fitting range in our study, which increases the uncertainty. Nonetheless, our results reconfirm the high-T_c superconductivity in $LaH_{10\pm\delta}$ reported in previous studies.[19,20]

In summary, we have successfully synthesized $LaH_{10\pm\delta}$ and confirmed its superconductivity at a high T_c ($\sim$250 K). For this purpose, we designed a simple sample-loading procedure in a symmetric DAC and measured the sample resistance using the standard four-probe method. The developed method reduces the technical difficulty of *in situ* syntheses and transport measurements at megabar pressures. Therefore, it can promote the research of near-room-temperature superconductors among metal superhydrides.

Some instruments used in this study are built for the Synergic Extreme Condition User Facility.

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