

Observation of the Josephson effect in superhydrides: DC SQUID based on (La,Ce)H_{10+x} with operating temperature of 179 K

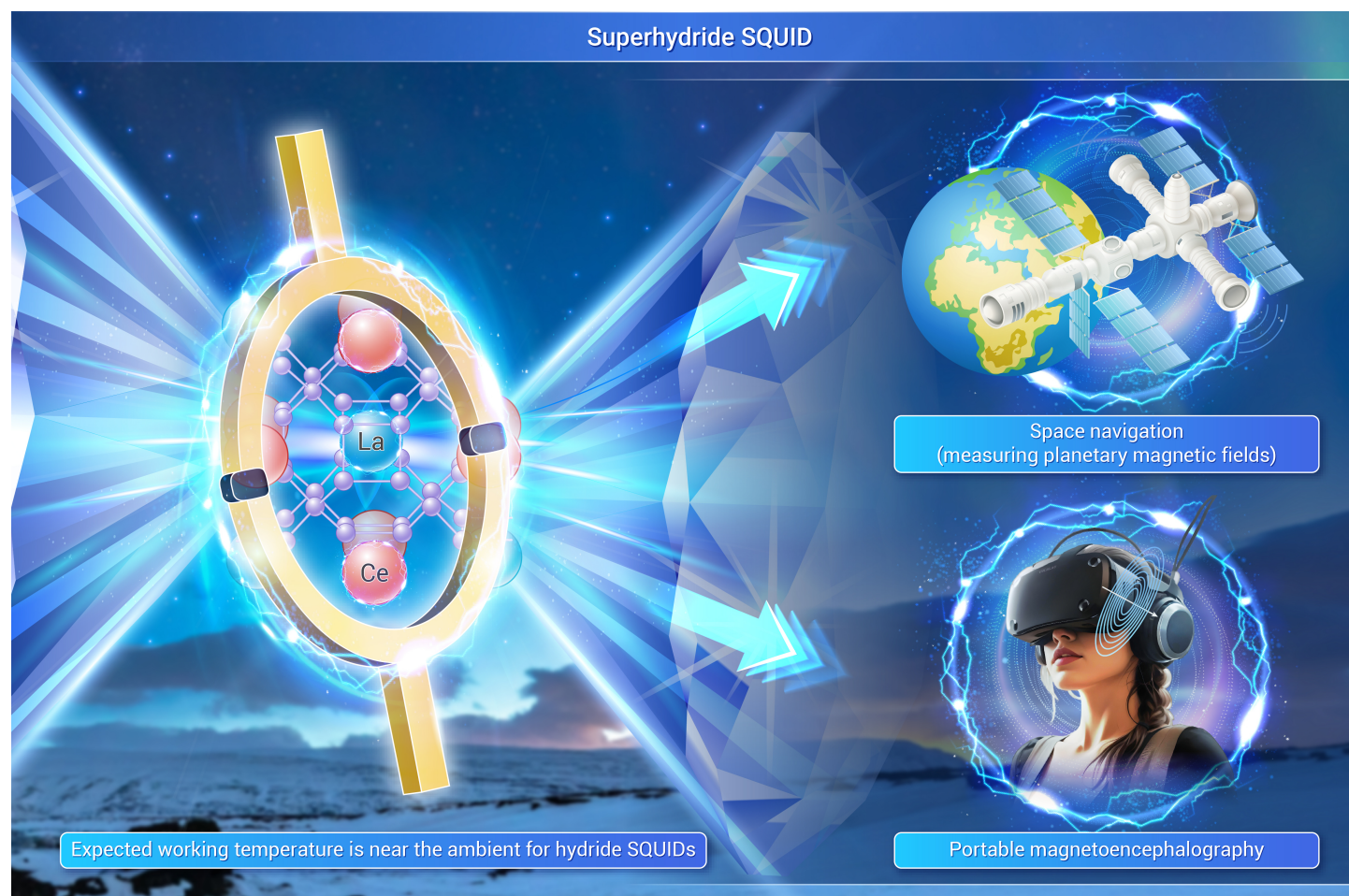
Dmitrii V. Semenov,^{1,7,*} Ivan A. Troyan,^{2,7} Di Zhou,^{1,7,*} Wuhao Chen,^{3,4} Ho-kwang Mao,^{5,6} and Viktor V. Struzhkin^{5,6,*}

*Correspondence: dmitrii.semenov@hpstar.ac.cn (D.S.); di.zhou@hpstar.ac.cn (D.Z.); viktor.struzhkin@hpstar.ac.cn (V.S.)

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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- We created SQUID (superconducting quantum interference device) with a record operating temperature of 179 K.
- Sensitivity of superhydride SQUIDs can be improved to 0.01 G, and the operating temperature can reach 240 K.
- More advanced applications of hydride SQUIDs can be envisioned by taking advantage of microfabrication tools.

Observation of the Josephson effect in superhydrides: DC SQUID based on $(\text{La,Ce})\text{H}_{10+x}$ with operating temperature of 179 K

Dmitrii V. Semenok,^{1,7,*} Ivan A. Troyan,^{2,7} Di Zhou,^{1,7,*} Wuhao Chen,^{3,4} Ho-kwang Mao,^{5,6} and Viktor V. Struzhkin^{5,6,*}

¹Center for High Pressure Science & Technology Advanced Research, Beijing 100193, China

²A.V. Shubnikov Institute of Crystallography of the Kurchatov Complex of Crystallography and Photonics (KKhF), Moscow 119333, Russia

³Quantum Science Center of Guangdong–Hong Kong–Macao Greater Bay Area (Guangdong), Shenzhen 518000, China

⁴Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China

⁵Shanghai Key Laboratory of Material Frontiers Research in Extreme Environments (MFree), Shanghai Advanced Research in Physical Sciences, Shanghai 201203, China

⁶Center for High Pressure Science and Technology Advanced Research, Shanghai, China

⁷These authors contributed equally to this work

*Correspondence: dmitrii.semenok@hpstar.ac.cn (D.S.); di.zhou@hpstar.ac.cn (D.Z.); viktor.struzhkin@hpstar.ac.cn (V.S.)

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Among known materials, hydride superconductors have the highest critical temperatures and are very promising as a basis for electronic sensors. Superconducting quantum interference device (SQUID), due to its unique sensitivity to magnetic fields, is the most important application of superconductors in microelectronics. In this work, we describe a direct current SQUID made of lanthanum-cerium superhydride $(\text{La,Ce})\text{H}_{10+x}$ (x is between -1 and $+2$) at pressure of 148 GPa, with operating temperature of 179 K and bias current of about 2 mA. When placing $(\text{La,Ce})\text{H}_{10+x}$ in a modulated magnetic field (frequency: 0.1–0.005 Hz, 5 Gauss), we observed generation of higher harmonics up to $18\nu_0$ and a periodic dependence of the sample resistance on the magnetic flux density $R \propto |\sin(\pi\Phi/\Phi_0)|$. We demonstrate that the $(\text{La,Ce})\text{H}_{10+x}$ SQUID with a size of $\sim 4\text{--}6\text{ }\mu\text{m}$, operates in the mode of low thermal fluctuations and can be used to detect magnetic fields below 0.1 G. Our findings pave the road to more advanced applications of the Josephson effect and SQUIDs made of hydride superconductors.

INTRODUCTION

Superconducting quantum interference device (SQUID) is a device based on superconducting (SC) loops containing at least one Josephson junction.^{1,2} Practically, it can be made from rings of a SC material with one or several weak links where the critical transition temperature (T_c) is lower than in the rest part of ring. Such device turns to be a very sensitive magnetometer that can be used to measure extremely weak magnetic fields as low as 5×10^{-18} T.^{3,4} SQUIDs can be designed on the basis of pure Nb or Al with oxide insulating Josephson junctions or weak links made of single walled carbon nanotubes.^{5,6} To maintain superconductivity, the entire device needs to operate under very low temperature, cooled with liquid helium. High-temperature SQUID sensors based on cuprates (e.g., yttrium barium copper oxide (YBCO)) are cooled by liquid nitrogen which is, from a practical point of view, easier than liquid helium cooling, but higher operating temperature leads to higher level of noise and less sensitivity than conventional He-temperature SQUIDs.^{7,8} Despite this, high-temperature SQUID sensors have many applications in biology including magnetoencephalography,⁹ magnetic marker monitoring,¹⁰ cardiology, magnetic resonance imaging in low fields.¹¹ Reduction in a thermal insulation thickness, permitted for liquid nitrogen cooling, enables the devices to be placed much closer to the sample under investigation, thus boosting the magnetic signal level. As we will see below, in some high-pressure diamond anvil cells, the sample and the SQUID sensor are separated by a physical barrier of only 5–6 mm, which is overcome by introducing inductive coupling using additional copper coils.

High-temperature SQUID sensors make it possible to detect weak magnetic fields of various organs (brain, stomach, heart), to study their electrical activity and its spatial distribution. Many SQUID applications are associated with physical research, for example, the creation of quantum superconducting qubits and computers based on them,¹² a scanning SQUID microscope,¹³ the study of the magnetic properties of materials, the search for the quadrupole moment of the electron,¹⁴ to make cryogenic particle detectors¹⁵

and in many other areas. As the history of SQUID technology shows, both types of SQUIDs – noisy high- T_c devices (based, for example, on cuprates) and precise low-noise low- T_c magnetometers have occupied their independent niches in the application market.

Problem of increasing the operating temperature of high- T_c SQUIDs rests on the search for new superconducting materials with a higher T_c . Fortunately, a kind of “hydride revolution” in superconductivity began in 2014, leading to the discovery of high- T_c superhydrides such as H_3S ,¹⁶ LaH_{10} ,^{17,18} which has a current record of $T_c = 250\text{ K}$, YH_6 ,^{19,20} ThH_{10} ,²¹ CeH_9 ,²² SnH_4 ,²³ $(\text{La,Ce})\text{H}_{9-10}$,^{24,25} and many others. The last one, lanthanum-cerium polyhydride, is one of the most convenient samples for high-pressure experiments: due to the stabilizing effect of Ce, its critical temperature $T_c = 190\text{--}200\text{ K}$ is achieved already at a pressure of 100–120 GPa.^{24,25} Such properties allow to work with large-sized samples and diamond anvils with a diameter of 100–150 μm . It was long thought that due to the microscopic size, the need to use diamond anvils and high-pressure anvil cells (DACs), high-temperature superconductivity in hydrides would not find practical applications.

In this work, we show that this is not the case, and already existing sample of La-Ce superhydride in a DAC demonstrates a pronounced direct current (DC) SQUID effect and can be used as a sensor of weak magnetic fields. It is conceivable that optimization of sample geometry by using microfabrication tools could lead to substantial improvement in SQUID sensitivity and control, thus opening many application areas for superhydrides.

MATERIALS AND METHODS

To load the high-pressure diamond anvil cell DAC H, consisting of a non-magnetic body made of 40HNU-VI alloy, diamond anvils with a culet diameter of 50 μm and sputtered Ta/Au electrical contacts (inset of Figure 1A), we used a particle of La_4Ce alloy with a thickness of 1 μm and a diameter of 45 μm . The La_4Ce alloy was prepared according to previously described procedure.²⁴ Ammonia borane (NH_3BH_3 , AB) was used as a hydrogen source. After laser heating, which consisted of several $\sim 0.3\text{ s}$ pulses of IR laser (wavelength is 1.04 μm), the pressure in DAC H increased from 137 to 148 GPa (Figure 1A).

The sample temperature was stabilized in the range of $179 \pm 0.5\text{ K}$ using a Lakeshore 335 temperature controller and insulated NiCr wire with a thickness of 50 μm and a resistance of about 100 Ω wound around the diamond anvil cell DAC H (Figure 1F). The current passing through this heater created an additional magnetic field, which should be attributed to interfering noise. Cernox 1030 thermometer (error is $\pm 0.2\text{ K}$) was glued by Al_2O_3 -based heat conductive adhesive on a DAC's rhenium gasket within 1 mm from the sample.

The magnetic field was generated using a Hantek signal generator (peak-to-peak amplitude was 10 or 20 V, maximum field in the solenoid $\approx 5\text{ G}$). The generator signal was also used as a reference for the SR830 lock-in amplifier (Stanford Research). Lock-in amplifier parameters: time constant 30 ms, sensitivity 200 mV, detection period: 100 ms. We used a frequency of 50 mHz and a second harmonic was 100 mHz. For DC measurements we used Keithley 6221 current source and Keithley 2182A nanovoltmeter, detection period was 100 ms. Sample resistance measurements were carried out in the delta

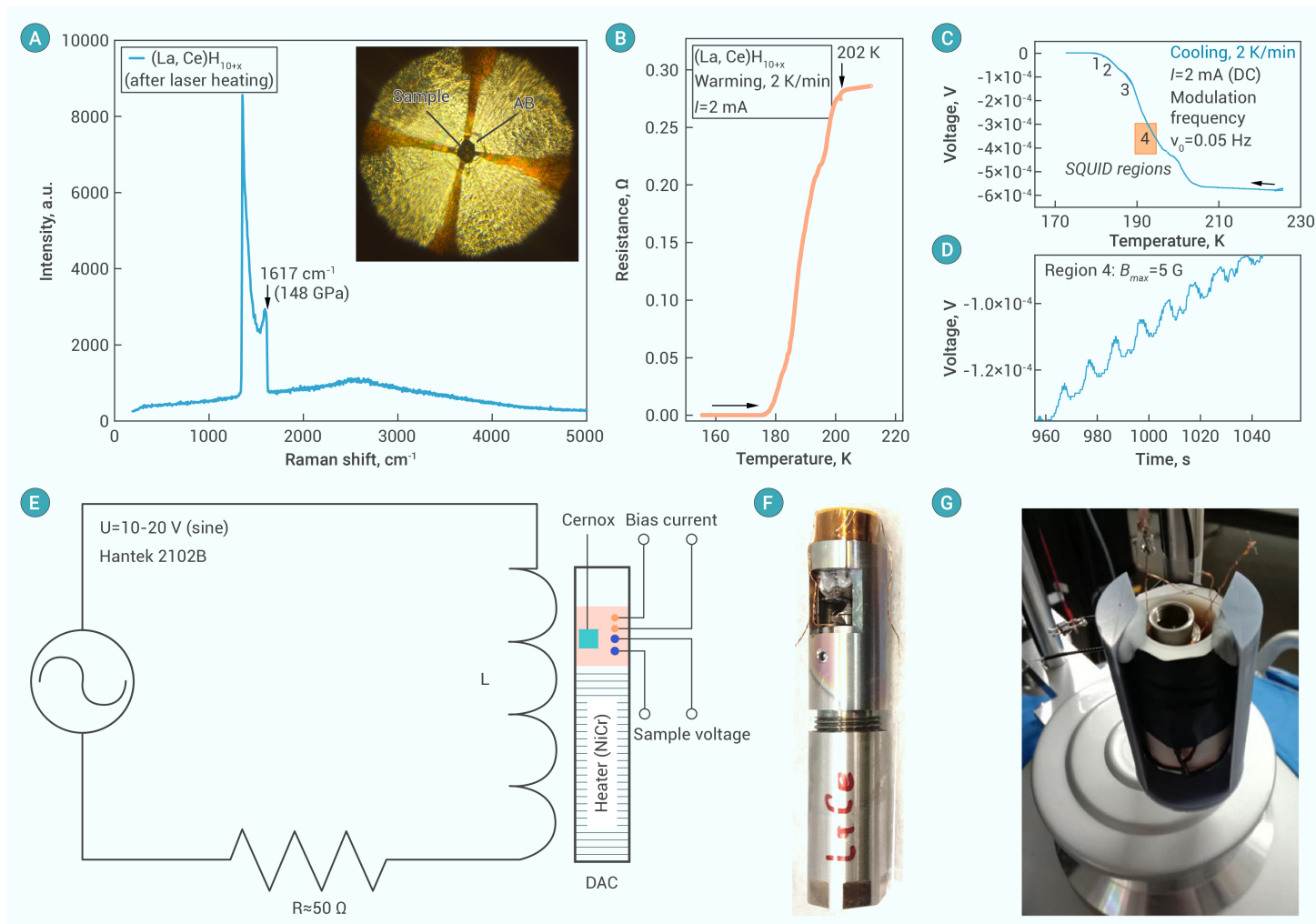


Figure 1. Properties of the $(\text{La, Ce})\text{H}_{10+x}$ sample in the DAC H and the scheme of measurements. (A) Raman spectrum of the sample after laser heating. The edge of the diamond Raman signal corresponds to a pressure of 148 GPa.²⁷ Inset: photo of the DAC's culet with compressed sample. (B) Superconducting transition in $(\text{La, Ce})\text{H}_{10+x}$ observed within the warming cycle. (C) Cooling of a $(\text{La, Ce})\text{H}_{10+x}$ sample in a magnetic field of ~ 5 G modulated by a low frequency of 0.05 Hz. To measure the voltage drop across the sample, we used a DC current of 2 mA. The modulation in the sample resistance appears only in a few temperature intervals: around 187 K, 182–184 K, 181–179 K etc. The most convenient interval for studying the DC SQUID effect is in the region of the lowest resistance around 179 K. (D) We zoomed in one of the regions of the voltage-temperature curve where pronounced generation of the second harmonic (0.1 Hz) is observed, and showed it as a function of time to emphasize the modulation of the response. (E) The scheme of the experimental setup. A Hantek 2102B signal generator was used to create a sinusoidal magnetic field in a solenoid "L". (F) The photo of the DAC H. (G) The photo of the DAC H in the solenoid before placing it in a liquid nitrogen dewar. The process of cooling and temperature stabilization was carried out in a nitrogen vapor.

mode.

RESULTS

DC measurements

High-pressure electrical diamond anvil cell DAC H with a hydride sample synthesized from a $\text{La}_{80}\text{Ce}_{20}$ alloy and ammonia borane was used in our experiments (Figure 1A). A sharp drop in electrical resistance at T_c (onset) = 200–205 K was observed in both heating and cooling cycles using DC delta mode (Figure 1B) and alternating current (AC) measuring circuits (Figure 3A). Considering that the found T_c is higher than it was determined in early works for cubic and hexagonal $(\text{La,Ce})\text{H}_{9+x}$,^{24,25} and also results of X-ray diffraction analysis of a hexagonal $(\text{La,Ce})\text{H}_{12}$ sample prepared in the same manner from $\text{La}_{86}\text{Ce}_{14}$ alloy and NH_3BH_3 (Figures 4D–F), we will further attribute the chemical formula $(\text{La, Ce})\text{H}_{10+x}$ to the studied compound (similar to LaH_{10+x} ²⁶).

Near the T_c , the polyhydride samples should contain many S-N-S contacts (N - normal metal, S - superconductor) in their composition due to the disordered structure and gradient of concentration of defects, hydrogen and, accordingly, the critical temperature. This was noted already in the very first years of research, for example in YH_6 .^{19,20} In particular, it manifests in a small linear magnetoresistance,^{23,28} high upper critical magnetic fields B_{c2} exceeding 200 T,²⁴ broad SC transitions in ternary hydrides, very short electron mean free path,²⁸ and other phenomena. In some situations, at a certain tempera-

ture close to T_c and at a bias current close to the critical one I_c , the S-N-S contact arrays will randomly form SQUID-like loops and circuits connected in a standard 4-electrode scheme. In this case, there will be several SQUID loops of different areas, $S_1, S_2, S_3, \dots$, which will work simultaneously (inset of Figures 2A & 4A–C). The maximum possible area of such loops is the area of the entire sample, which in our case ($d \approx 45 \mu\text{m}$) is equal to $15.9 \times 10^{-10} \text{ m}^2$. One magnetic flux quantum $\Phi_0 = 2.068 \times 10^{-15} \text{ Wb}$ will be achieved in the field of $1.3 \mu\text{T} = 0.013 \text{ G}$, which is approximately the sensitivity limit of the SQUID magnetometer in our experiments. By increasing the sample size to 100 μm , it is theoretically possible to achieve a sensitivity of $\approx 300 \text{ nT}$. Thus, to observe the SQUID effect in superhydrides, there is no need to create a special sample topology. This effect can be seen in many hydride samples prepared for transport measurements during cooling/warming in a weak modulated magnetic field (Figures 1C–D). In the case of $(\text{La, Ce})\text{H}_{10+x}$, we observed the appearance of complex oscillations of the resistance in certain temperature intervals near T_c (Figure 1D). Further analysis indicates the appearance of the DC SQUID effect in the sample (Figure 2).

We examined synthesized superconducting $(\text{La,Ce})\text{H}_{10+x}$ sample in the DAC H at 148 GPa and found that in a certain range of temperature $179 \pm 0.5 \text{ K}$ and bias current 1–2.5 mA, there is an unusually strong sensitivity of electrical resistance and the sample voltage drop to a weak low-frequency magnetic field of the solenoid "L" (Figures 1D & 2). A low frequency of 0.1–

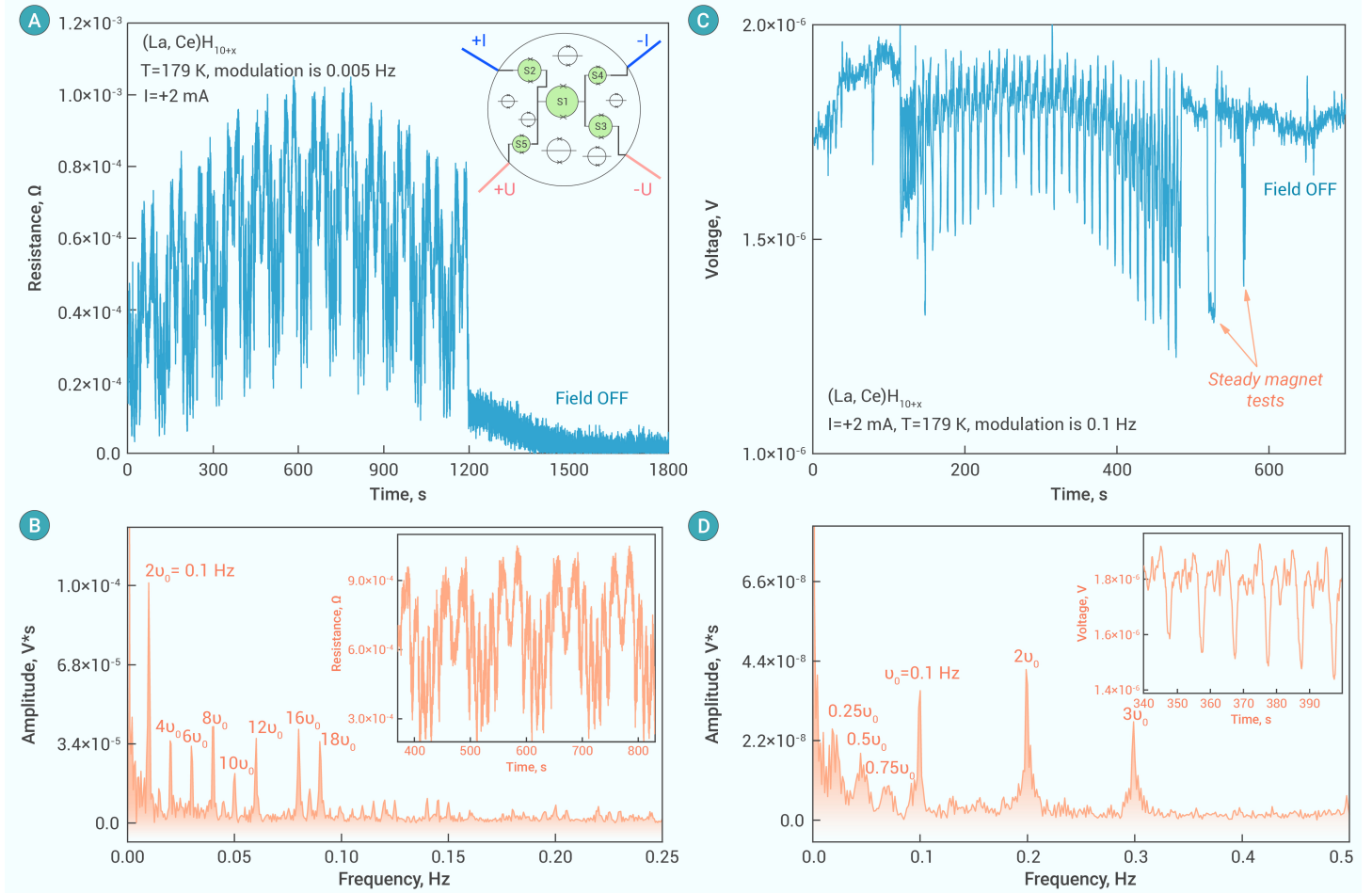


Figure 2. The DC SQUID effect and generation of higher harmonics in the $(\text{La, Ce})\text{H}_{10+x}$ sample at the pressure of 148 GPa and the temperature of 179 ± 0.5 K. The external magnetic field was generated by a sinusoidal current passing through a solenoid with a frequency of (A) 0.005 Hz and (C) 0.1 Hz. The bias current through the SQUID was +2 mA in both cases. Panel (A) shows the sample resistance measured in delta mode²⁹ with a period of 100 ms. The “Field OFF” zone corresponds to a turned off external magnetic field. The inset shows a qualitative drawing explaining the presence of multiple SQUID circuits (areas $S_1, S_2, S_3, \dots$) in the sample in different temperature/current intervals. The figures (B, D) show the Fourier analysis of the resulting complex periodic signal, which demonstrates the presence of pronounced peaks of higher harmonics, characteristic of the SQUID effect in periodic magnetic fields. Insets: the analyzed signals $R(t)$ and $U(t)$. The pronounced signal asymmetry in panels (C) and (D) is explained by the diode effect in the hydride sample.³⁰ Peaks at $\sim 0.025, 0.05, 0.075$ Hz in Figure D correspond to non-integer flux quantization.

0.005 Hz was used to suppress inductive effects while keeping in mind also possible future applications in biology.³¹ The observed SQUID effect does not depend on the direction of the DC current ($I_{\text{bias}} = -2$ mA, Figure S2) and is seen in delta mode resistance measurements as well (Figure 2A).²⁹ Direct measurements of the magnetic field of the solenoid show that in the mode of maximum signal amplitude (nominal peak-to-peak $\Phi_0 = 20$ V), the low-frequency signal generator allows creating a field of about $B_{\text{max}} = 5$ Gauss in the solenoid, measured by a Hall sensor. The sensitivity of the DAC H and the estimated signal-to-noise ratio (Table S1), reaching $(S/N)_{\text{max}} \approx 83$, show that we can detect weaker magnetic fields of the order of 0.1 Gauss.

Distinctive feature of SQUID circuits is the extremely high sensitivity of their electrical resistance (or critical current) with respect to a weak magnetic field (B), and the intrinsic periodic dependence of measured voltage on the magnetic flux (within RSJ-model³²⁻³⁴)

$$R = \frac{U}{I_{\text{bias}}} = \frac{R_J I_c}{I_{\text{bias}}} \sqrt{\left(\frac{I_{\text{bias}}}{2I_c}\right)^2 - \cos^2\left(\pi \frac{\Phi}{\Phi_0}\right)}, \quad (1a)$$

where $\Phi = BS$ - is a magnetic flux passing through a SQUID circuit,³⁵ R_J - is a resistance of the Josephson junction and I_c - its critical current, while I_{bias} - is a DC current used for measurements. Since the experiments were performed at the optimized current $I_{\text{bias}} = 2I_c = 2$ mA (Figure 2A), where the modulation amplitude was greatest, the formula (1a) simplifies

$$R = \frac{U}{I_{\text{bias}}} = \frac{R_J}{2} \left| \sin\left(\pi \frac{\Phi}{\Phi_0}\right) \right|. \quad (1b)$$

Due to the modulation of the external magnetic field in our experiment, $B(t) = B_{\text{max}} \sin(2\pi \nu t + \varphi_0)$. For simplicity, let us set the phase shift $\varphi_0 = 0$, then we can use the convergent Taylor series

$$R(t) = \frac{U(t)}{I_{\text{bias}}} \propto \left| \sin\left(\frac{\pi''\Phi_{\text{max}}}{\Phi_0} \sin(2\pi \nu t)\right) \right| = \left| \frac{\pi''\Phi_{\text{max}}}{\Phi_0} \sin(2\pi \nu t) - \frac{1}{6} \left(\frac{\pi''\Phi_{\text{max}}}{\Phi_0} \sin(2\pi \nu t)\right)^3 + \frac{1}{120} \left(\frac{\pi''\Phi_{\text{max}}}{\Phi_0} \sin(2\pi \nu t)\right)^5 + \dots \right|, \quad (2a)$$

where Φ_{max} - a maximum magnetic flux passing through a SQUID circuit, ν - a modulating field frequency. If we assume that $\pi\Phi_{\text{max}}/\Phi_0 = 1$, then the expression (2a) can be simplified further and we can understand where the higher harmonics in the frequency spectrum come from (Figure 2B).

$$R(t) \propto |0.88 \sin(2\pi \nu t) + 0.039 \sin(6\pi \nu t) + 5.21 \cdot 10^{-4} \sin(10\pi \nu t) \dots| \quad (2b)$$

Since we have asymmetric SQUID which also demonstrates pronounced diode effect (Figure S12), as well as non-zero phase shifts ($\varphi \neq 0$) and $\pi\Phi_{\text{max}}/\Phi_0 \neq 1$ (Taylor expansion still converges), it becomes obvious that the experimental signal $U(t)$ or $R(t)$ can contain many different even and odd harmonics, which is indeed observed (see Figures 2, S2-S4 & S13-S15). The occurrence of subharmonics (Figure 2D, $\nu = 1/4 \nu_0, 1/2 \nu_0, 3/4 \nu_0$), corresponding to the non-integer flux quantization, is also noted in a number of

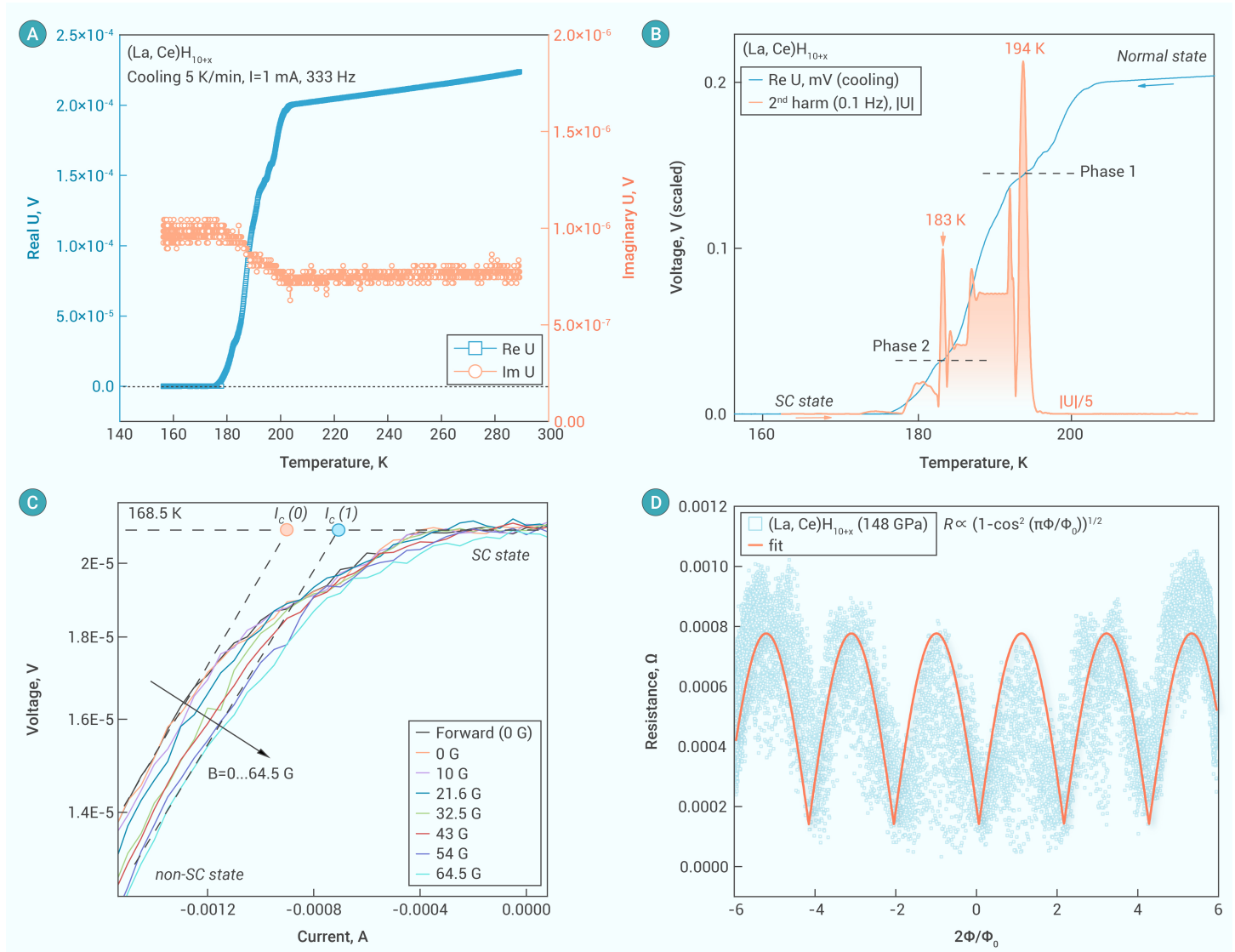


Figure 3. The AC transport study of the $(\text{La, Ce})\text{H}_{10+x}$ sample in DAC H at 148 GPa in a modulated low-frequency magnetic field. A four-electrode van der Pauw⁴¹ circuit was used (A) The temperature dependences of the real (Re U, blue curve) and imaginary (Im U, orange curve) components of the voltage on the sample. The cooling cycle with a rate 5 K/min in zero magnetic field. For measurements, a sinusoidal current of 1 mA (RMS, Keithley 6221) with a frequency of 333 Hz was used. (B) Absolute voltage $|U| = (\text{Re}U)^2 + (\text{Im}U)^2$ on the second harmonic ($2\nu_0$) of the external field modulation frequency $B_{\text{max}} \approx 5$ G, $\nu_0 = 0.05$ Hz (orange curve) and its temperature dependence compared to the real AC voltage component taken from panel "a" (ReU, blue curve). It can be seen that the signal peaks of the 2nd harmonic correspond to the "shelves" of the $U(T)$ curve and probably relate to the changing nature of the grain boundaries: from N-N to S-N and S-S. (C) Voltage-current characteristics of the sample at lower temperature, 168.5 K. $I_c(0)$ corresponds to the critical current in the absence of a magnetic field, whereas $I_c(1)$ is the critical current in the maximum field studied (64.5 G). The resulting $U-I$ curves are similar to ones of a weak-link based YBCO SQUID magnetometer described in⁴². (D) The dependence of the $(\text{La, Ce})\text{H}_{10+x}$ SQUID resistance on magnetic flux Φ in the flux quantum Φ_0 units calculated under the assumption of characteristic radius of the SQUID $r \sim 3$ μm . Raw data depending on the signal generator voltage are given in Figure S11.

cases and is often observed for inhomogeneous samples, in a series of connected SQUIDs, or if the SQUID lies on a metal plate.^{36,37}

The Little-Parks effect³⁸ may be another reason for observing small periodic oscillations in the resistance of a cylindrical superconductor. The amplitude of oscillations in the "dirty" limit is given by the formula³⁹

$$\frac{\Delta T_c(B)}{T_c} = \frac{\Delta R}{(dR/dT)_{T_c}} = 0.73 \frac{\xi_0 l_e}{r^2} \left(n - \frac{\Phi_0}{\Phi} \right)^2, \quad (3)$$

where ΔR – is amplitude of resistance oscillations, dR/dT – is the slope of $R(T)$ function, ξ_0 – is the coherence length at 0 K, and l_e – is the electron mean free path. For superhydrides, all of the listed characteristic lengths are on the order of nanometers: $\xi_0 \approx 1.5$ nm for LaH_{10} ,⁴⁰ and $l_e \approx 1.6$ nm for similar ternary hydride $(\text{La, Nd})\text{H}_{10}$.²⁸ Considering that in our case $dR/dT \approx 0.013$ Ω/K , we come to the conclusion that the amplitude of the Little-Parks resistance oscillations is about several $\mu\Omega$ for micron loops (r), which is approximately 100–500 times less than the values observed in our experiment (Figure 2A, 0.5–0.7 m Ω). Thus, the Little-Parks effect is too small to explain the observed strong resistivity oscillations in the $(\text{La, Ce})\text{H}_{10+x}$ sample.

Finally, it is necessary to comment the possible influence of multiple S-N-S interfaces presented in the sample on the generation of higher harmonics. There is no doubt that such interfaces exist and cause a smooth transition to the SC state in the range from 202 K to 175 K as can be seen from Figure 1B. In this temperature range, the resistance gradually decreases due to the constant growth of the superconducting fraction in S-N-S weak links on a current path between electrodes. Thus, at any point $T_c(\text{offset}) < T < T_c(\text{onset})$ of the $R(T)$ curve, we are dealing with multiple S-N-S interfaces. However, their existence itself does not lead to a high sensitivity of the sample's resistance to the external weak periodic magnetic field, which is observed only in several relatively narrow temperature regions of a few Kelvins wide (Figures 1B–D & S1).

AC measurements

The presence of higher harmonics in the SQUID spectrum allows us to use the SR830 lock-in amplifier to measure the voltage drop across the sample in AC mode (Figure 3A), for example, at the second harmonic, which is almost always the most pronounced. Indeed, at a current on the sample $I_{\text{bias}} = +2$

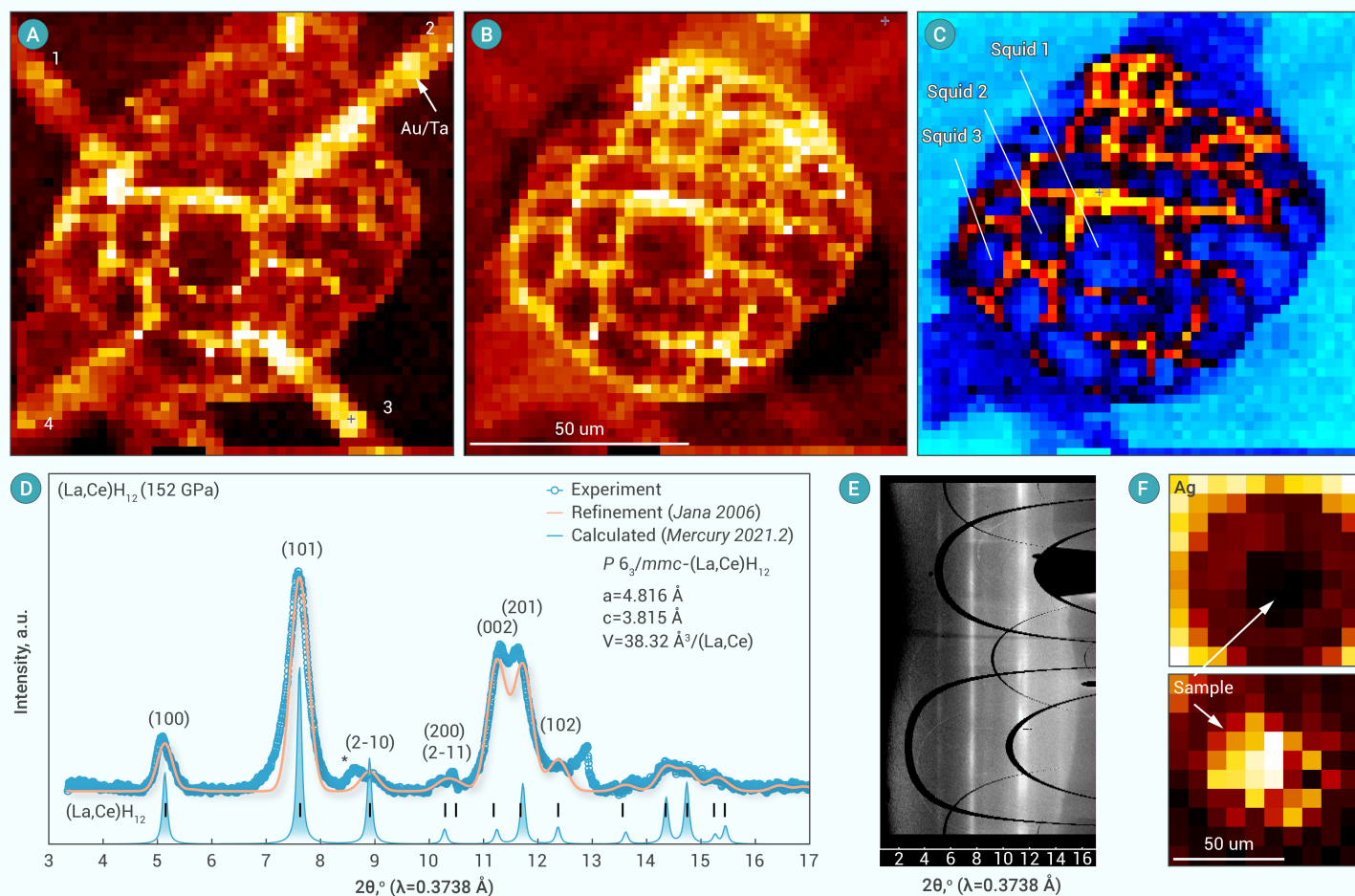


Figure 4. X-ray diffraction studies of polyhydrides in special DACs with a wide opening angle, synthesized via laser heating of metals and alloys with ammonia borane (A-C) Distribution of Ba-Si polyhydrides synthesized at around 40 GPa. High resolution XRD mapping clearly shows Au/Ta electrodes 1-4 (A), as well as round patterns of higher polyhydride phases with weak links (B, C: "squid 1-3") formed along the isothermal lines near the laser focal spot. The color map corresponds to the intensity of the first diffraction peak of a higher polyhydride BaSiH_x. (D-E) X-ray diffraction (XRD) pattern of La-Ce hydride synthesized from La₉₆Ce₁₄ alloy and NH₃BH₃ at 152 GPa in a special XRD DAC. Powder X-ray diffraction analysis and the Le Bail refinements of the unit cell of (La,Ce)H₁₂ phase at 152 GPa. Blue points mark experimental data, the orange line – is the refinement, and the blue bottom line – is predicted XRD of $P6_3/mmc$ -(La,Ce)H₁₂. Asterisks mark unexplained reflections. (E) X-ray diffraction image ("cake"). (F) Material distribution map for the Lenz lens (Ag) and (La,Ce)H₁₂ hydride (sample).

mA, pronounced generation of the 2nd harmonic is observed from the frequency of the modulating magnetic field ($\nu_0 = 50 \text{ mHz}$, Figure 3B). Peaks of 2nd harmonic generation occur at the temperature of N-S to S-S contact transitions at the grain boundaries of various superconducting phases. At least two or three different superconducting phases with different T_c 's are present in the sample. These phases inevitably form during high-pressure and high-temperature synthesis of superhydrides in DACs and are possibly characterized by a different hydrogen content: for example, (La, Ce)H₉ and (La, Ce)H₁₀.^{22,24,25}

In the vicinity of $T_c(\text{offset})$, at 180 K, the generation of the 2nd harmonic is associated with the SQUID effect in the sample (Figure 3B), while the remaining signal is probably related to the diode effect accompanying asymmetrical DC SQUID circuits.³⁰ This explains the fact that in the normal and superconducting state, the generation of the 2nd harmonic is not observed despite the continued operation of the solenoid with the same frequency of 50 mHz. Therefore, sensing of a signal at the second harmonic can be used to detect SC transition, diode and SQUID effects in hydride superconductors.

The study of critical currents and U - I characteristics was carried out at temperatures significantly lower than 179 K in order to decrease electrical resistance of the sample, avoid problems with heating and to ensure that a significant part of the U - I characteristic was superconducting (flat). At temperatures below 179 K, the SQUID effect in the (La, Ce)H_{10+x} sample is weakly expressed (Figure S8), which leads to a weak dependence of the critical current on the external field of the solenoid up to 64.5 G. Nevertheless, dependence of the critical current on the field is also observed at 168.5 K

(Figure 3C) providing another argument in favor of presence of Josephson junctions in the sample.

Finally, Figure 3D & S11 demonstrate the classical periodic dependence of the SQUID signal on the applied magnetic field in coordinates of the generator voltage connected to the solenoid or magnetic flux Φ . It is very similar to what was observed for the first YBCO ceramic SQUID in 1987.⁴³ This relationship is based on the data in Figure 2A. The signal amplitude changes due to heating and sample temperature drift when passing such a significant current (2 mA) through DC SQUID normal resistance of Josephson contacts $R_N/2 = 0.2 - 1 \text{ m}\Omega$ at 179 K. The signal period corresponds to a magnetic field of about 1.7 – 1.8 G, and we can estimate the radius of the superconducting circuit as $r \sim 2-3 \text{ }\mu\text{m}$.

DISCUSSIONS

Inhomogeneities of the superconducting phase play an important role in the observed SQUID and diode effects. In particular, in the range of 194-200 K, no peculiarities in the behavior of the 2nd harmonic are observed, although part of the sample is in a superconducting state (Figures 3B-C). Figures 2 & S1-S2 also show that the observed effect is caused by modulation of the external magnetic field of the solenoid and disappears when it is turned off ("Field OFF"). The DC SQUID effect exists in a wide range of modulation frequencies from 0.1 to 0.005 Hz, in a bias current range from 1.5 to 2.5 mA (Table S1), and can be reproduced in different superhydrides, for instance, in (La,Sc)H₁₂⁴⁴ and in La₄H₂₃.⁴⁵ In all cases, generation of higher harmonics up to 18 ν_0 is found. The (La, Ce)H_{10+x} sample exhibits high sensitivity to an external

magnetic field of a permanent magnet located within 0.3–0.5 m from the sample (Figure 2C, “steady magnet tests”).

Proposed idea of random formation of hydride rings during laser heating of ammonia borane in DACs can be illustrated by a relatively large and well-studied (50×50 X-ray diffraction map, 2 μm step) sample of Ba-Si polyhydrides (Figures 4A–C). Since the synthesis in that symmetric electrode DAC with a wide opening angle was carried out by a similar way of pulsed laser heating of a BaSi sample and ammonia borane, we believe that the results in the case of La-Ce hydrides will be qualitatively identical. In Figures 4B–C, characteristic round patterns of hydride phases with a diameter of up to 15 μm are clearly visible. They correspond to isothermal lines around the focal spot of IR laser used for the sample heating. Presence of such superconducting hydride rings of (La,Ce)H_{10+x} causes the observed DC SQUID effect in the DAC H.

As previously mentioned, the asymmetric DAC H with $d = 15.3$ mm is intended for transport measurements only and cannot be investigated by X-ray methods. Therefore, we prepared another sample for XRD (Figures 4D–F), synthesized at 152 GPa in a DAC with wide opening angle, using a similar alloy La₈₆Ce₁₄ and ammonia borane. As a result, we obtained a previously unknown La-Ce hydride, the diffraction pattern of which (Figure 4D) can be explained by the hexagonal structure $P6_3/mmc$ -(La,Ce)H₁₂ with the unit cell parameters $a = 4.816$ Å, $c = 3.815$ Å, $V = 38.32$ Å³/(La,Ce), which corresponds to a ratio of heavy atoms to hydrogen of 1:12. The unusual for $P6_3/mmc$ ratio $c/a = 0.79$ indicates that the heavy atom sublattice may be described by a different hexagonal space group. It should be noted that hydrides with similar composition have been synthesized previously: these are LaH₁₂¹⁷ and (La,Sc)H₁₂.⁴⁴ However, given the previous work on the La-Ce system, which led to the discovery of (La,Ce)H_{9–10},²⁴ and considering high $T_c(\text{onset}) > 200$ K, in this paper we designate the studied compound as (La,Ce)H_{10+x}, where x can take values between -1 and $+2$.

One of the important parameters that describe the efficiency of a SQUID magnetometer is the so-called screening parameter $\beta_L = 2I_c L / \Phi_0$, where L – the inductance of the system, I_c – the Josephson junction critical current. The β_L parameter for an optimized SQUID is usually of the order of unity.³⁵ Assuming the ideal case of a single-turn coil with a diameter of 45 μm and a height of 1 μm, we obtain the inductance $L_{\text{max}} = 70 - 100$ pH and $\beta_L > 100$. Moreover, if the SQUID circuit is smaller than the (La,Ce)H_{10+x} sample diameter, then the inductance decreases significantly. So, if we have a ring with a radius of 3 μm, then $L \approx 10$ pH and $\beta_L \sim 10$. Not surprisingly, our “natural” DC SQUID turns out to be not the most optimal one due to the operating current being too high. The parameters found are close to those for YBCO SQUID with weak links (scratches on thin film).⁴⁵

It is generally believed that for a SQUID to operate effectively, two basic conditions should be met³⁵:

(1) Quantum interference dominates thermal fluctuations:

$$L < L_f = \frac{\Phi_0^2}{4\pi^2 k_B T} = 44 \text{ pH at } 179 \text{ K}, \quad (4)$$

where T – the operating temperature, k_B – the Boltzmann constant. This condition is satisfied in our case for fairly small SQUID circuits of less than 20 μm, but it limits the possibilities for further increasing the sensitivity of superhydride SQUIDs due to their high operating temperature, which can already reach 240 K.⁴⁷

(2) The Josephson coupling energy should be greater than the thermal energy:

$$\Gamma = \frac{2\pi k_B T}{\Phi_0 I_0} = \frac{I_{th}}{I_0} = \frac{7.5 \mu A}{I_0} \ll 1, \quad (5)$$

where I_{th} – the current of thermal fluctuations. Considering that the operating current $I_{\text{bias}} = 1 - 2.5$ mA in our case, we come to the conclusion that the (La,Ce)H_{10+x} DC SQUID operates in the mode of small thermal fluctuations and retains the potential to reduce the working current by 10–100 times. Despite the noise and heterogeneity of the described hydride SQUIDs, the possibility of their use in combination with compact thermoelectric coolers at temperatures of -25 – -30°C , as we recently showed for (La,Sc)H₁₂,⁴⁴ opens ways to the creation of portable magnetometers on Li batteries for on-site field research.

CONCLUSIONS

We discovered the DC SQUID effect in lanthanum-cerium polyhydride (La,Ce)H_{10+x} at temperature of 179 ± 0.5 K and pressure of 148 GPa, caused by a random inhomogeneous spatial distribution of superconducting gap in a microscopic sample. Periodic dependence of the sample resistance on the magnetic field allows to estimate the characteristic size of the SQUID circuit as $d \sim 4$ – 6 μm, with a normal resistance of the Josephson “weak” links being about $0.2 - 1$ mΩ at the operating temperature. Pronounced sample response to an external modulated magnetic field of ~ 5 G is observed when passing a direct bias current of $1 - 2.5$ mA. The screening parameter $\beta_L = 2I_c L / \Phi_0 \sim 10$ in our device and can be further improved. Considering the signal-to-noise ratio S/N up to 83, the DC SQUID based on a high-pressure diamond anvil cell DAC H can be used to detect weak magnetic fields down to 0.1 G. The sensitivity of superhydride SQUIDs of similar size can be improved at least by a factor about 10 to 0.01 G, and the operating temperature can reach 230–240 K.⁴⁴

Moreover, even more advanced applications could be envisioned by taking advantage of microfabrication tools to prepare more controllable and sophisticated superhydride-based SQUID devices. Such devices will certainly bring the quantum properties of SQUIDS close to room temperature, allowing the study of Josephson junction-based qubits in thermoelectrically cooled devices.

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AUTHOR CONTRIBUTIONS

D.S. and D.Z. conceived the original idea. D.S., D.Z., W. C. and I. T. performed experiments. D.S. and V.V.S. analyzed the data and wrote the manuscript. V.V.S. and H.K.M. supervised the project. All the authors discussed the results and offered useful inputs. All authors contributed to and approved the manuscript

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

The authors declare that the main data supporting our findings of this study are contained within the paper and Supporting Information. All relevant data are available from the corresponding authors upon request. Raw data is available on the GitHub website: <https://github.com/mark6871/LaCeH10/tree/SQUID>.

SUPPLEMENTAL INFORMATION

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