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Superconductivity above 200K Observed in Superhydrides of Calcium

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Searching for superconductivity with T_c near room temperature is of great interest both for fundamental science & potential applications. Here we report the experimental discovery of superconductivity with maximum critical temperature(T_c) above 210 K in calcium superhydrides, the third type hydride experimentally showing superconductivity above 200K in addition to sulfur hydride & rare earth hydride system. The materials are synthesized at the synergetic conditions of 160~190 GPa and ~2000K using diamond anvil cell combined with in-situ laser heating technique. The superconductivity was studied through in situ high pressure resistance measurements in applied magnetic field for the sample quenched from high temperature while maintained at the synthesized pressure. The upper critical field was estimated to be ~268T while the GL coherent length is ~11 Å. The in situ x ray diffractions with synchrotron suggest that the synthesized calcium hydrides are primarily composed of CaH₆ while there also exist other calcium hydrides with different hydrogen.

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Introduction

The superhydrides received growing attentions recently because of the high temperature superconductivity^[1]. It was suggested that superhydrides are likely to be a step toward metallic hydrogen since the “chemically precompressed” hydrogen in the superhydrides can decrease the critical pressure required for the metallization^[1-3]. Because of high phonon frequencies and strong electron phonon coupling, high temperature superconductivity was suggested in hydrogen rich materials. Sulfur hydride is one of examples, in which the high T_c superconductivity was reported both theoretically & experimentally at Megbar level pressures^[4, 5]. In addition, alkali earth, rare earth and other superhydrides are theoretically suggested to possess high temperature superconductivity at high pressures^[6-10]. Those metal superhydrides favor to form hydrogen rich coordination such as clathrate like cage structures at high pressure where the metal ions are located in the center of the H clathrats and act as carrier donor. The occupation of the unfilled anti-bonding σ^* orbitals of the H_2 molecules by the electrons from the metal ions would enhance to dissociate the H_2 molecules hence to form H clathrats. Recently rare earth Lanthanum (or Yttrium) hydrides are also experimentally reported to be superconductive with T_c exceeds 200 K^[12-16]. However, there are no experimental observations for superconductivity above 200 K so far in alkaline earth superhydrides, in spite of the superconductivity with $T_c \sim 20$ K was reported in barium hydrides^[17]. Here, we report the experimental realization of high T_c superconductivity in calcium superhydrides synthesized at high pressure and high temperature conditions. The superconductivity with $T_c \sim 210$ K at 160 ~190 GPa was observed. Hence in addition to sulfur hydrides, rare earth hydrides this is the third type of superconducting hydrides with T_c above 200K..

Experiment

The diamond anvil cell techniques are used for both synthesis & measurements of the calcium hydrides. The diamond anvils are of optical pure quality with culet diameter of 100 μm beveled to 300 μm for the experiments. The electrodes for resistance measurements are embedded in the sample chamber before high pressure high temperature synthesis. The experiments are conducted in two steps: (I) synthesis of the calcium hydrides at high pressure high temperature; (II) the follow up measurements of superconductivity for the sample quenched from high temperature but remained at the same pressure. The T301 stainless steel served as gaskets that are prepressed from 250 μm to ~ 20 μm in thickness at about 20 GPa. A hole of 300 μm in diameter was drilled at the center of imprint. The hole filled with fine insulating cubic boron nitride (cBN) powder mixed with epoxy that was pressed with anvils to form a solid layer of ~ 15 μm in thickness. A hole of 70 μm in diameter was drilled at the center of the solid cBN layer to serve as the sample chamber. The Pt foils with the thickness of 0.5 μm were deposited on the surface of the culet as the inner electrodes. The gold wire was attached to the Pt foil to serve as the outside electrodes. The calcium specimen with a shape of 30 μm in width *30 μm in length and 2 μm in thickness was stacked on the inner electrodes. A flake of ammonia borane filled into the sample chamber plays the role of hydrogen source (hydrodizer) while it also the pressure transmitting medium^[14]. The sample loading as well as electrodes performance are conducted in the glove box filled with flowing Ar gas with 1ppm oxygen or water trace to avoid moisture or contamination. The setups are followed the ATHENA procedure reported Ref 18.

The sample was first applied to the pressure of 160~190 GPa followed by heating

at $\sim 2000\text{K}$ for $\sim 30\text{min}$. The heating was performed with a pulse laser beam of 1064nm wave length. The spot of laser beam is about $5\text{ }\mu\text{m}$ in diameter with power of 20 W . The heating temperature was estimated by fitting the black body irradiation spectra. The heated sample was quenched from high temperature while maintained at high pressure. A piston cylinder type anvil cell composed of BeCu was adopted in the experiments. The synthesized sample compressed within diamond anvil cell was put into a MagLab system to perform the electric conductivity measurements using a Van der Pauw method with 1 mA applied current. The MagLab system can provide synergetic extreme environments with temperatures from 300 K to 1.5 K and a magnetic field up to 9 T ^[19]. Pressure was calibrated by the shift of the first order Raman edge frequency from the cutlet of diamond^[20, 21].

The synchrotron x-ray diffraction experiments in the diamond anvil cell were carried out at GSECARS of the Advanced Photon Source at the Argonne National Laboratory. The x-ray with $\lambda = 0.3344\text{ \AA}$ was focused down to $\sim 3\text{ }\mu\text{m}$ diameter spot on the sample. The symmetric diamond anvil cell was used to generate pressure with bevel diamond anvils ($100/300\mu\text{m}$) and rhenium gasket indented to $25\mu\text{m}$. Samples were loaded into the pressure chamber without the insulated layer of cBN and Pt electrodes that were used for resistive measurements. Calcium hydrides was synthesized in situ at 175 GPa with laser heating at 2000K . The sample pressure in these synchrotron X ray diffraction experiments has been determined by both the shift of Raman edge frequency from the cutlet of diamond and the equation of state for rhenium. The X-ray diffraction images are converted to two dimensional diffraction data with Dioptas²⁰.

Results & Discussions

Fig. 1(a) displays the image of the sample assembly. The dotted red square is the sample shape and the four gray dotted regions are the inner electrodes. Fig. 1(b) shows the measurements of resistance as function of temperature at 160 GPa for sample A. The resistance curves almost coincide for both the cooling and warming cycles. The resistance drops at around 210 K and approaches to zero at low temperature suggesting that the superconducting like transitions take place in the calcium superhydrides. Fig. 2 shows the resistance measurements by application of magnetic fields for sample A. It is seen that the whole transition curves shift to low temperature with the critical temperature gradually suppressed by the applied field, in consistent with the nature of superconductivity. The inset of Fig. 1(b) displays the enlarge view of the derivative of resistance over temperature around the transition region, from which the T_c^{onset} of 210 K is estimated at right side upturn point. In addition to the first transition at ~ 210 K, there are also several drop kinks at ~ 180 K and ~ 160 K as shown in Fig.1(b). These drop kinks imply multistep superconducting transitions that are supported by the broaden transition curves shown in Fig.2. In the context of calculation, the calcium hydrides such as CaH_6 , CaH_{10} , CaH_{12} etc are stable or metastable at high pressure and show high T_c superconductivity^[2, 6, 11]. Hence it is likely that these multistep transitions should be attributed to calcium hydrides with different hydrogen amount, which are probably synthesized due to inhomogeneity of either pressure or hydrogen. It is natural that there exists large pressure gradient in pressure cell at megabar pressure, while the hydrogen inhomogeneity likely arises from the inhomogeneous laser heating to ammonia borane. We synthesized couples of samples to optimize the single transition quality either by reducing sample size in

order to improve pressure homogeneity or to heat sample in a more homogeneous scanning manner. Fig. 3(a) presents the resistance as function of pressures measured at 185 GPa for samples B and C, where one step sharp with $T_c \sim 200$ K are achieved. The superconductivity is supported by the measurements at applied magnetic field as shown in Fig. 3(b).

To estimate the upper critical field $H_{c2}(0)$, the superconductivity as function of magnetic field was investigated based on sample C. The T_c values are determined with the criteria of the T_c^{onset} , the temperature at 90% and 50% of normal state resistance, respectively. By linear fitting the $H_{c2}(T)$, the slope of $dH_{c2}/dT|_{T_c}$ was obtained to be -1.976 T/K for the T_c^{onset} , -1.726 T/K for the 90% of normal state resistance and -1.389 T/K for the 50% of normal state resistance, respectively. Using the Werthamer-Helfand-Hohenberg (WHH) formula of $\mu_0 H_{c2}(T) = -0.69 \times dH_{c2}/dT|_{T_c} \times T_c$, the $H_{c2}(0)$ value was calculated to be 268 T, 227 T and 179 T for the criteria of T_c^{onset} , the 90% and the 50% of normal state resistance, respectively. The Ginzburg Landau (GL) formula of $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)(1 - (T/T_c)^2)$ is also used to estimate the upper critical field at zero temperature. As shown in Fig. 4 the fitting of the $\mu_0 H_{c2}(T)$ by GL formula gives a value of $H_{c2}(0)$ ranging from 131 T to 195 T using criteria of T_c^{onset} , the temperature at 90% and 50% of normal state resistance, respectively. They are comparable to those reported in LaH₁₀^[12]. Using the obtained value of $H_{c2}(0)=131\sim 268$ T, one can roughly estimate the GL coherence length ξ to be 11~16 Å via the equation of $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi^2$, where $\Phi_0 = 2.067 \times 10^{-15}$ Web is the magnetic flux quantum.

The possible superconducting phases are investigated by high pressure x-ray diffraction experiments and it was suggested that the primary phase of the

superconducting sample is composed of $Im\bar{3}m$ phase of CaH_6 as shown in Fig. S1-3. We became aware during preparing the paper that an independent work by Ma *et al.* was carried with the similar results^[23].

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Author Contributions

Research Design & Supervision: C.Q.J.; high pressure synthesis and in situ resistance measurements: Z.W. L., X.H., C.L.Z., S.J.Z., Y.T.J., S.M.F., Y.W.L.,X.C.W., R.C.Y, J.F.Z., C.Q.J; in situ synchrotron experiments: L. H. W., M.Y.Y., Z.S.Z., V.B.P., S.C., H.Z.L., manuscript writing: Z.W.L., X.C.W. and C.Q.J. All authors contributed to the discussions.

Competing interests: The authors declare no competing interests.as defined by Nature Portfolio, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Figure Captions:

Fig. 1 (a) The image of the specimen assembly. (b) The temperature dependence of resistance $R(T)$ measured at 160 GPa for sample A. The multiple steps in the transition region imply there might be phases with different hydrogen amount in the synthesized calcium superhydrides. The inset is the enlarged view of the derivative of resistance over temperature (dR/dT) where the ~ 210 K T_c^{onset} is determined as the upturn point at the right side.

Fig. 2 The resistance as a function of temperature measured at different magnetic field for sample A. The arrows are attributed to the phases with different hydrogen amount in the calcium superhydrides. The inset is the enlarged view of the resistance curves around the transition region of the 210 K phase.

Fig. 3 (a) The temperature dependence of resistance measured for samples B and C at 185 GPa showing one step transition. (b) Resistance curves measured under different magnetic field for sample C.

Fig. 4 The Ginzburg Landau fitting for the $H_{c2}(T)$ shown with the solid lines. The stars represent the $H_{c2}(0)$ values calculated via WHH model. The inset of Fig. 4 is the critical field $H_{c2}(T)$ as a function of T_c with the T_c values determined by the criteria of the T_c^{onset} , 90% and 50% of normal state resistance, respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Supplementary materials

Superconductivity above 200K Observed in Superhydrides of Calcium

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Five strong peaks are observed, which of three can be indexed with lattice

parameters of $a=b=c=3.3497 \text{ \AA}$ and the systematic absence of hkl implies the possible space group of $Im\bar{3}m$; these results agree with the predicted for CaH_6 at 150 GPa ($a=b=c=3.501 \text{ \AA}$). Thus, we use the crystal structure of $Im\bar{3}m\text{-CaH}_6$ as the initial model to carry out the refinement for our diffraction data. After the other two strong unknown peaks marked by stars were excluded, the refinement converged smoothly to $R_{wp}=4.3\%$ and $R_p=3.9\%$. It is suggested that the main phase is possibly CaH_6 , which might respond to the superconducting transition observed with T_c exceeding 200 K. However, if we compare the X-ray diffraction data with the theoretically predicted model of $C2/m$ phase of CaH_{12} under 150 GPa, it is found that the main peaks also seem to match the predicted peaks shown with the dark yellow line. In addition, for the sample D, it shows superconducting transition at 189 K and 185 GPa as shown in Fig. S3, which is lower than the calculated T_c of CaH_6 but comparable with the T_c value predicted from CaH_{12} . Therefore, we cannot rule out the possibility that the high temperature superconductivity found in our sample arises from the other calcium hydrogen phases.

Fig. S2.1. The diffraction image plate with diffraction rinks.

Fig. S2.2. The upper is the image along the azimuthal lines of the diffraction image. The main panel presents the diffraction pattern with integrated area shown with the square in Fig. S2.1.

Fig. S3. The temperature dependence of resistance measured for sample D at 185 GPa. The inset is the enlarged view of the derivative of resistance over temperature (dR/dT).