Enhancing the three-dimensional electronic structure in 1111-type iron arsenide superconductors by H-substitution

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ABSTRACT

The 1111-type iron arsenide hydride CaFe$_{1-x}$Co$_x$AsH was synthesized by high-pressure solid-state reaction, and its electronic structure and superconducting properties were investigated. Bulk superconductivity was observed at $x = 0.09$–0.26. A maximum superconducting critical temperature ($T_c^{\text{max}}$) of 23 K was observed at $x = 0.09$. These values are in agreement with those of CaFe$_{1-x}$Co$_x$AsF. The calculated Fermi surface of CaFeAsH has a small three-dimensional (3D) hole pocket around the $\Gamma$ point. This is a result of weak covalent bonding between the As 4$p$ and H 1$s$ orbitals. No such covalency exists in CaFeAsF, because the energy level of the F 2$p$ orbital is sufficiently deep to inhibit overlap with the As 4$p$ orbital. The similar superconductivities of CaFe$_{1-x}$Co$_x$AsH and CaFe$_{1-x}$Co$_x$AsF are explained on the nesting scenario. The small 3D hole pocket of CaFe$_{1-x}$Co$_x$AsH does not significantly contribute to electron excitation. These findings encourage exploration of hydrogen-containing 1111-type iron-based materials with lower anisotropies and higher $T_c$ applicable to superconducting wires and tapes.
I. INTRODUCTION

Since the discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ (critical temperature ($T_c$) = 26 K), the physical properties of new families of iron pnictide superconductors have been extensively investigated.\textsuperscript{2-7} LnFeAsO ($Ln =$ lanthanide)\textsuperscript{1,8-11} and AeFeAsF ($Ae =$ alkali earth),\textsuperscript{12,13} or the so-called 1111-type oxyarsenides and fluoroarsenides, respectively, are typical such families. They possess a ZrCuSiAs-type crystal structure, composed of alternately stacked FeAs anti-fluorite-type conducting layers and LnO/AeF fluorite-type insulating layers. Stoichiometric 1111-type families undergo structural and magnetic transition with decreasing temperature. Superconductivity arises when these transitions are suppressed, by carrier doping of the FeAs layers. Carrier doping modes for these 1111-type families are classified as “direct” and “indirect” doping, according to their substitution sites. The former involves elemental substitutions in FeAs layers, such as cobalt or nickel substitution at iron sites.\textsuperscript{14-17} The latter involves aliovalent ion substitutions in LnO/AeF layers, such as substitution at oxygen sites with fluorine.

We recently reported the high-pressure synthesis of the hydrogen-substituted 1111-type compounds CaFeAsF$_{1-x}$H$_x$ ($x = 0.0-1.0$)\textsuperscript{18} and LnFeAsO$_{1-x}$H$_x$ ($x = 0.0-0.5$).\textsuperscript{18-20} Hydrogen is incorporated as H$^-$ at F$^-$ or O$^{2-}$ sites, in the blocking layers of CaFeAsF or LnFeAsO, respectively. The high solubility of hydrogen ($x < 0.5$) in 1111-type oxyarsenides results in a wide superconducting dome of $0.05 < x < 0.4-0.5$. The valence state and ionic radius of hydrogen are
close to those of fluorine. However, their solubility toward oxygen and their pressure dependence of $T_c$ are rather different.\textsuperscript{21} This implies that the large spatial spread and softness of hydride electrons lead to different chemical bonding states in 1111-type iron pnictides and the fluoride-1111 material.

In this paper, we report the superconductivity of 1111-type CaFeAsH, which is induced by Co-substitution at the Fe site. The maximum $T_c = 23$ K and the extent of the superconductivity (SC) region in the $x$-$T$ diagram are similar to those of Co-substituted CaFeAsF. The effect of hydrogen on 1111-type iron pnictides is discussed, by comparing the electronic structures of CaFe$_{1-x}$Co$_x$AsH and CaFe$_{1-x}$Co$_x$AsF.

\section*{II. EXPERIMENTAL}

CaFe$_{1-x}$Co$_x$AsH was synthesized by the solid-state reaction of CaAs, CaH$_2$, Fe$_2$As and Co$_2$As, using a belt-type high-pressure anvil cell. The specific reaction was:

\begin{equation}
\text{CaAs} + \text{CaH}_2 + (1-x) \text{Fe}_2\text{As} + x\text{Co}_2\text{As} \rightarrow 2\text{CaFe}_{1-x}\text{Co}_x\text{AsH}
\end{equation}

CaH$_2$, CaAs, Fe$_2$As and Co$_2$As were prepared from their respective metals. CaH$_2$ was synthesized by heating metallic Ca in a H$_2$ atmosphere. All starting materials and precursors were prepared in a glove box under a purified Ar atmosphere (H$_2$O and O$_2$ < 1 ppm). The starting material mixture was placed in a BN capsule, with a mixture of Ca(OH)$_2$ and NaBH$_4$ acting as an excess hydrogen source.\textsuperscript{22} The mixture was heated at 1273 K under 2 GPa for 30 min. The crystal phase and structure
were identified by powder X-ray diffraction (XRD), using Mo $K_{\alpha}$ radiation at room temperature. The sample was first ground into a fine powder, and placed in a glass capillary ($\varphi$ 0.5 mm). XRD measurements were recorded in transmission mode, to reduce the effects of preferential crystallite orientation. Rietveld refinement of XRD patterns was performed using TOPAS software. The chemical composition was determined by an electron-probe micro analyzer (EPMA; JEOL model JXA-8530F), equipped with a field-emission-type electron gun and wavelength dispersive X-ray detectors. Micron-scale compositions within the main phase were probed at ten individual focal points, and the results were then averaged. The temperature dependence of the DC electrical resistivity ($\rho$) at 2–200 K was measured using the conventional four-probe method, using Ag paste as the electrodes. Magnetic susceptibility ($\chi$) was measured with a vibrating sample magnetometer (Quantum Design). $\chi$ was measured on bulk and powdered samples and the data of the powder were adopted. Non-spin-polarized density functional theory (DFT) calculations with Perdew-Burke-Ernzerhof functional and the projected augmented plane-wave method were implemented in the Vienna ab initio Simulation Program (VASP) code. A conventional cell containing two chemical formula units, and structural parameters obtained by the interpolation of experimental values, were used. The effect of partial Co-substitution at the Fe site was taken into account through the virtual crystal approximation. The plane-wave basis-set cutoff was 600 eV. For Brillouin-zone integrations to calculate the total energy and DOS, $20 \times 20 \times 10$ Monkhorst-Pack grids
of $k$ points were used. The projected density of states (PDOS) was obtained by decomposing the charge density over the atom-centered spherical harmonics with the same Wigner-Seitz radius $r = (3V_{\text{cell}}/4\pi N)^{1/3}$, where $V_{\text{cell}}$ and $N$ are the unit-cell volume and number of atoms per unit cell, respectively.

III. RESULTS

Crystal structure

Figure 1(a) shows the powder XRD pattern of CaFe$_{1-x}$Co$_x$AsH, with $x$ value of 0.12. Except for minor peaks arising from Fe metal and unknown impurities, most peaks can be indexed to a ZrCuSiAs-type structure of $P4/nmm$ symmetry, as shown inset in Fig. 1(a). Figure 1(b) shows the analyzed $x$ value in CaFe$_{1-x}$Co$_x$AsH, as a function of ($x_{\text{nom}}$) in the starting mixture. The analyzed $x$ value is proportional to $x_{\text{nom}}$, and its deviation from $x_{\text{nom}}$ indicates the segregation of a Co-rich impurity phase. The EPMA analysis indicates the existence of an impurity of composition CaFe$_{1.85\pm0.12}$Co$_{1.03\pm0.11}$As$_{1.82\pm0.05}$, in addition to Fe metal. The volume fraction of Co-rich impurity phase estimated by analyzing the EPMA mapping images (200 $\mu$m $\times$ 200 $\mu$m, 400 $\times$ 400 points) linearly increases with increasing $x$ and reaches up to 27% at $x = 0.308$. Figure 1(c) and (d) show variations in the CaFe$_{1-x}$Co$_x$AsH lattice parameters $a$ and $c$, respectively, as a function of analyzed $x$. These parameters for CaFe$_{1-x}$Co$_x$AsF are also shown for comparison. The CaFe$_{1-x}$Co$_x$AsH $a$-axis
length increases with increasing Co-substitution, whereas the $a$-axis length decreases. The $a$-axis dimensions of CaFe$_{1-x}$Co$_x$AsH are comparable to those of CaFe$_{1-x}$Co$_x$AsF, whereas the $c$-axis lengths are $\approx 35$ pm shorter than those of CaFe$_{1-x}$Co$_x$AsF. Figure 1(e), (f) and (g) show the As distance from the Fe plane ($h_{As}$), the Ca distance from the H/F plane ($h_{Ca}$), and the distance between the Ca and As planes ($d_{Ca-As}$), respectively. While $h_{Ca}$ and $d_{Ca-As}$ remain largely constant, $h_{As}$ decreases with increasing $x$. This indicates that the monotonic decrease of $c$-axis length with increasing $x$ originates from the decrease in $h_{As}$. The different $h_{As}$ ($< 2$ pm), $h_{Ca}$ ($\approx 7$ pm) and $d_{Ca-As}$ ($\approx 12$ pm) values of CaFe$_{1-x}$Co$_x$AsH and CaFe$_{1-x}$Co$_x$AsF are independent of Co-substitution. This also supports the conclusion that the different $c$-axis lengths originate from the decrease in $d_{Ca-As}$.

Superconducting Properties

Figure 2(a) and (b) show the temperature dependence of the electrical resistivity ($\rho$) for CaFe$_{1-x}$Co$_x$AsH, with $x = 0.04$–0.12 and 0.17–0.31, respectively. The anomaly in the $\rho$-$T$ curves due to structural or magnetic transitions is observed at $T_{anom} \approx 80$ K for $x = 0.02$. $T_{anom}$ decreases to $\approx 55$ K at $x = 0.04$. These samples exhibit a small $\rho$ decrease at $\approx 20$ K, but zero resistivity is not observed. Figures 2(c) and (d) show the temperature dependence of the magnetic susceptibility ($\chi$) for CaFe$_{1-x}$Co$_x$AsH, with $x = 0.04$–0.12 and 0.17–0.31, respectively. The $4\pi\chi$ value of near 0 at $x = 0.02$ and 0.04 indicates that the $\rho$ decrease of these samples arises from the local inhomogeneity of Co. As $x$ increases $\geq 0.07$, zero resistivity is attained and the onset $T_c$ reaches a maximum ($T_c^{max}$) of 23 K at
$x = 0.07$. Further Co-doping causes a monotonic decrease in $T_c$. Superconductivity is eventually completely suppressed at $x = 0.31$. Figure 2(e) shows the shielding volume fraction (SVF) evaluated from the gradient of the $M$ vs. magnetic field ($H$) curve at 2 K and the volume fraction of the Co-rich impurity phase estimated by EPMA. The SVF was evaluated by utilizing the volume fraction of contained phases in samples estimated by EPMA on the assumption that the density of the Co-rich impurity phase was the same as that of CaFe$_2$As$_2$ whose constituent element and composition is very close to the Co-rich impurity phase. The SVF value of > 26% for samples of $0.09 \leq x \leq 0.26$ indicates bulk superconductivity. Here, we mention that the possibility of superconductivity derived from the Co-rich impurity. Since there are no step on the $4\pi\chi$-$T$ curves in the superconducting region, superconductivity observed here is probably caused by a unity phase unless superconducting domes of the others phases accidentally coincide. Moreover, the volume fractions of the Co-impurity phase are smaller than SVF values in the range of $0.09 \leq x \leq 0.26$. Consequently, it is concluded that observed superconductivity is caused by CaFe$_{1-x}$Co$_x$AsH. Figure 2(f) shows $T_{anom}$ and $T_c^{onset}$ values from the $\rho$-$T$ curves, as a function of $x$. These values for CaFe$_{1-x}$Co$_x$AsF are also shown for comparison.\textsuperscript{12} $T_c$-dome values for CaFe$_{1-x}$Co$_x$AsH are in the range of $x = 0.09$–0.26, with $T_c^{max} = 23$ K. The $T_c^{max}$ and the extent of the SC region are comparable to those of CaFe$_{1-x}$Co$_x$AsF. This implies that the superconducting properties are not significantly changed by replacing the blocking layer anion from $F^-$ to $H^-$. 
Electronic structures

Figure 3(a) compares the calculated DOS of CaFeAsF and CaFeAsH. Energy bands located around the Fermi level ($E_F$) are mainly composed of Fe 3$d$ states. The DOS of these two compounds are comparable at $-2 < E < 2$ eV. Below the Fe 3$d$ bands, the energy bands are mainly composed of As 4$p$ states, which are located at $-6 < E < -2$ eV. In CaFeAsF, fluorine 2$p$ states form further bands at $-7.5 < E < -5.5$ eV, without admixing with the orbitals of other atoms. On the other hand, in CaFeAsH, hydrogen 1$s$ states energetically overlap well with As 4$p$ states. Ca orbitals contribute at $-2 < E < -5$ eV, which suggests that they admix with the H1$s$ orbital. Figure 3(b) shows band dispersion and the contribution of Fe 3$d$ orbitals. In CaFeAsF, there are three hole pockets around the Γ point, and two electron pockets around the M-point. The dispersion and orbital contribution of the electron-pockets and two of the three hole-pockets are comparable with those of CaFeAsH. However, one hole-like band in CaFeAsH crosses the $E_F$ in the Γ-Z path, as shown by the red line in Fig. 3(b) (which corresponds to the crystallographic c-axis). As a consequence, the dominant orbital nature in the hole pocket changes from Fe 3$d_{yz/zx}$ in CaFeAsF, to Fe 3$d_{x^2-y^2}$ and 3$d_{z^2}$ in CaFeAsH. Figure 3(c) shows the Fermi surfaces of CaFeAsH and CaFeAsF. They each have two hole pockets (denoted as $a_2$ and $\gamma$) and two electron pockets with the same orbital nature. The primary difference between them is the shape of the smallest hole pocket (denoted as $a_1$) around the
Γ to Z line, which is indicated by the red line. A sandglass-shaped pocket exists in CaFeAsH, compared with a cylinder-shaped pocket in CaFeAsF. Figure 4 shows the Fermi surfaces of CaFe$_{1-x}$Co$_x$AsH and CaFe$_{1-x}$Co$_x$AsF, with $x = 0.10$ which corresponds to the optimal electron doping level. As described in the supplementary information (Figs. S1 and S2 of [29]), a rigid band model is valid for Co-substitution. That is, the band structure of CaFe$_{1-x}$Co$_x$As(H, F) is similar to that of CaFeAs(H, F), with the $E_F$ shift corresponding to the number of electron supplied from Co. The $E_F$ shift results in the smallest hole-pockets in both systems remaining largely unchanged by Co-doping. However, two hole pockets diminish and two electron pockets slightly enlarge with increasing Co content. This robustness of the $\alpha_1$ hole pocket against Co-doping is attributed to the dispersion of the band producing the $\alpha_1$ hole pocket being larger than that of the electron, $\alpha_2$ or $\gamma$ hole pocket.

IV. DISCUSSION

The difference in the electronic structures of CaFeAsH and CaFeAsF is first discussed. The differences in the calculation are the structural parameters ($a$, $c$, $z_{As}$ and $z_{Ca}$) and the anion species within the blocking layer (H$^-$ or F$^-$). However, the band structure calculated for CaFeAsF using the structural parameters for CaFeAsH does not reproduce the Fe 3$d$ band crossing the $E_F$ in the Γ-Z path (See Supplemental Material, Fig. S3 of [29]). Therefore, the three-dimensional (3D) nature originates from the contribution of the hydrogen 1$s$ state, despite it being located far from the
Figure 3(a) shows that the hydrogen 1s states energetically overlap well with As 4p, and slightly overlap with the Ca components. The fluorine 2p states do not energetically overlap with the Ca components. This overlap results in the formation of weak covalent bonding. The covalency of energetically overlapped H 1s and As 4p states is investigated next. Figure 5(a) shows the contribution of As 4p and H 1s to the band dispersion. In CaFeAsH, hybridization of As 4p with the H 1s orbital is apparent in some parts of the bands. This indicates the presence of covalent bonding between them, despite that they are separated by 334 pm. No such covalency is observed in CaFeAsF, because each orbital contribution is distinctly separated between F 2p and As 4p states.

The effect of this covalent bonding on the Fermi surface is discussed next. The change in the band structure of CaFeAsH near the $E_F$ is explained by the schematic orbital configuration shown in Fig. 5(b). The H 1s orbital covalently bonds with the As 4pz orbital, the latter which is overlapped with the lobes of the Fe 3d_{x^2-y^2} and 3d_{z^2} orbitals. The H 1s orbital weakly overlaps with Ca 4s/3d orbitals. The As 4p orbitals mediate the inter-layer bonding of the Fe 3d_{x^2-y^2} and 3d_{z^2} orbitals in adjacent FeAs layers. This results in the 3D electronic structure observed in Fig. 3(b). The dispersion of As 4p_z-derived bands along the $\Gamma$-Z direction depends on the dimensionality of the crystal structure.30 For example, the band width along $\Gamma$-Z is $\approx$ 0 eV in Ca$_4$As$_2$O$_6$Fe$_2$As$_2$ with its thick blocking layer, while it is 0.4 and 2 eV in LaFeAsO and BaFe$_2$As$_2$, respectively. In BaFe$_2$As$_2$, the energy band with Fe 3d_{z^2} character crosses the $E_F$, forming the 3D hole pocket. The 3D
electronic nature of BaFe$_2$As$_2$ is apparent from its electron transport properties.\cite{31} In CaFeAsH, the 3D electronic nature is caused by bonding passing through the As-H-Ca bond. Covalent bonding between H and As is also reflected in the crystal structure of CaFeAsH: the shorter $d_{\text{Ca-As}}$ distance in CaFe$_{1-x}$Co$_x$AsH in Fig. 1(e) results from the decreased As-H separation. Electrons in the As 4$p_z$ orbital are partly utilized in bond formation. Thus, the Fe-As bond in CaFeAsH weakens and lengthens relative to that in CaFeAsF, as shown in Fig. 1(g).

Spin fluctuations arising from the Fermi surface nesting between the hole and electron pockets are a plausible explanation for the mediation of superconductivity in iron pnictides.\cite{32,33} The primary difference in the Fermi surfaces of CaFeAsH and CaFeAsF is the dimensionality of the $\alpha_1$ hole pocket around the $\Gamma$-Z line, as indicated by red line. The former is 3D and the latter is two-dimensional (2D). Both hole pockets are smaller, and their curvatures are much larger than those of the electron pockets. This means the $\alpha_1$ hole pocket does not contribute effectively to the nesting, \emph{i.e.}, the development of spin fluctuation. The size and shape of the $\alpha_1$ hole pocket remain largely unchanged up to $x = 0.1$, indicating that its contribution to superconductivity is small.

This hydrogen effect leads us to further consider its role in hydrogen-substituted $Ln$FeAsO. Hydrogen substitution effectively forms 3D Fermi surfaces, even for materials with 2D crystal structures. However, this change in Fermi surface does not affect their superconducting properties.
Hydrogen is an effective dopant for electron generation via oxygen site substitution, similarly to fluorine in \( LnFeAsO \). This indicates that incorporating hydrides enhances the 3D nature of 1111-type compounds, without suppressing their superconductivity.

V. SUMMARY

Superconductivity was observed in \( CaFe_{1-x}Co_xH \), and its properties were compared with those of \( CaFe_{1-x}Co_xAsF \). The maximum \( T_c \) and width of the superconducting dome of \( CaFe_{1-x}Co_xAsH \) are almost the same as those of \( CaFe_{1-x}Co_xAsF \). The calculated electronic structure of \( CaFeAsH \) differs from that of \( CaFeAsF \). The former has a 3D hole surface, with a highly 3D nature. This fact is caused by covalent bonding between energetically overlapped As 4p and H 1s bands. This 3D hole surface does not interfere with superconductivity because poor nesting between this small hole surface and electron surfaces causes the unfavorable development of excitations, such as spin and/or charge. Hydrogen incorporated within the blocking layer acts as an indirect electron dopant, without interfering with the superconductivity.
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CaFe$_{1-x}$Co$_x$AsF were prepared by solid state reaction of CaF$_2$, CaAs, Fe$_2$As and Co$_2$As in an evacuated silica tube at 1273K. The samples were ground into a powder and placed in a glass capillary ($\phi$ 0.5 mm) and XRD using Mo $K_a$ radiation at room temperature was measured by transmission mode. Their structure parameters were obtained by the rietveld analysis of XRD patterns.

See Supplemental Material at [URL will be inserted by publisher] for calculated electronic structures of CaFe$_{1-x}$Co$_x$AsF and CaFe$_{1-x}$Co$_x$AsH.
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FIGURE CAPTIONS

FIG. 1. (Color online) Structural details of CaFe$_{1-x}$Co$_x$AsH. (a) Powder XRD pattern of CaFe$_{0.88}$Co$_{0.12}$AsH. Red and black traces indicate observed and Rietveld-fitted patterns, respectively. The differences between them (blue) and Bragg positions of the main phase (green) and Fe impurity (wine-red) are also shown. Reflections from unknown phases are denoted by orange asterisks. (b) Analyzed $x$ content as a function of $x_{\text{nom}}$. (c) and (d) Lattice parameters $a$ and $c$, respectively, as a function of $x$. (e), (f) and (g) Fe-As bond length, Ca-(H,F) bond length and distance between the FeAs and blocking layer ($d_{\text{Ca-As}}$), respectively, as a function of $x$.

FIG. 2. (Color online) Electronic and magnetic properties of CaFe$_{1-x}$Co$_x$AsH. (a) and (b) $\rho$-$T$ profiles for $x = 0.02$–0.12 and 0.17–0.31, respectively. (c) and (d) Zero-field cooling (ZFC) $4\pi\chi$-$T$ curves measured on powdered samples under the magnetic field (H) of 10 Oe for $x = 0.02$–0.12 and 0.17–0.31. (e) SVF estimated from $M$-$H$ curves at 2 K and 10 Oe (red circle) and the volume fraction of Co-rich impurity (black line and triangle) (f) $x$-$T$ diagram of CaFe$_{1-x}$Co$_x$AsH compared with data reported for CaFe$_{1-x}$Co$_x$AsF.\textsuperscript{28}

FIG. 3. (Color online) Calculated electronic structures of CaFeAsH and CaFeAsF. (a) Total DOS and PDOS of CaFeAsH (left) and CaFeAsF (right). (b) Band structures along directions of high
symmetry in the Brillouin zone. Thick bands (blue) show the amounts of Fe-$d_{xy}$, $d_{yz/zx}$, $d_{x^2-y^2}$ and $d_{z^2}$ character. (c) Cross sections of Fermi surfaces in the $k_z = 0$ (top) and $k_x = k_y$ (bottom) planes.

FIG. 4. (Color online) Cross sections of Fermi surfaces of CaFe$_{0.9}$Co$_{0.1}$AsH and CaFe$_{0.9}$Co$_{0.1}$AsF, in the $k_z = 0$ (top) and $k_x = k_y$ (bottom) planes.

FIG. 5. (Color online) Contribution of arsenic, hydrogen and fluorine atomic orbitals to the electronic structures of CaFeAsH and CaFeAsF. (a) Thickness of bands shows the amounts of As-$p$ (green), H-$s$ (red) and F-$2p$ (purple) character. (b) and (c) Schematics showing the configurations of the H-$1s$, As-$4p$, Fe-$3d_{x^2-y^2}$ and -$3d_{z^2}$ orbitals.
FIG. 1
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