

Iron-based superconductivity extended to the novel silicide LaFeSiHF. Bernardini,¹ G. Garbarino,² A. Sulpice,³ M. Núñez-Regueiro,³ E. Gaudin,⁴ B. Chevalier,⁴ M.-A. Méasson,³ A. Cano,^{4,*} and S. Tencé⁴¹*Dipartimento di Fisica, Università di Cagliari, IT-09042 Monserrato, Italy*²*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, Boîte Postale 220, 38043 Grenoble, France*³*CNRS, Université Grenoble Alpes, Institut Néel, 38042 Grenoble, France*⁴*CNRS, Université Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France*

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We report the synthesis and characterization of the novel silicide LaFeSiH displaying superconductivity with onset at 11 K. We find that this pnictogen-free compound is isostructural to LaFeAsO, with a similar low-temperature tetragonal to orthorhombic distortion. Using density functional theory we show that this system is also a multiband metal in which the orthorhombic distortion is likely related to single-stripe antiferromagnetic order. Electrical resistivity and magnetic susceptibility measurements reveal that these features occur side by side with superconductivity, which is suppressed by external pressure.

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Introduction. Iron-based superconductors (Fe-based SCs) provide an unprecedented playground for the investigation of high- T_c superconductivity. These systems belong to a huge family of compounds and recurrently display the following key features (see, e.g., [1,2] for recent reviews). From the structural point of view, they have FeX layers in which the Fe atoms form a square lattice that is sandwiched between two ($\sqrt{2} \times \sqrt{2}$) $R45^\circ$ shifted lattices of X ($=$ P, As, Se, Te, S). This leads to a quasi-two-dimensional (quasi-2D) multiband Fermi surface that mainly originates from the Fe 3d orbitals. In addition, the parent compounds often display anti-ferromagnetic (AFM) order inducing a lattice distortion [3–5] that is generally preempted by the so-called nematic transition [2]. In the prototypical case of $R\text{FeAsO}$ (R = rare earth), for example, this specifically corresponds to single-stripe AFM order [also called $(\pi, 0)$ order] and a square-to-rectangular distortion of the Fe layers. These features advocate for the so-called s_{\pm} superconducting gap symmetry and a spin-fluctuation pairing. This superconductivity can be induced by carrier doping resulting from either chemical substitutions or physical pressure [6]. From a more methodological point of view, the electronic band structure and the magnetic orders found in Fe-based SC can be reasonably well described by means of density functional theory (DFT) based calculations as the electronic correlations often remain relatively weak.

The search for novel Fe-based SCs has been naturally extended to systems in which the FeX layer contains group-IV elements; in particular, the nontoxic Ge. Thus, MgFeGe, for example, has been identified as isostructural and isoelectronic to the LiFeAs compound but displaying no superconductivity [7–9]. Evidence for superconductivity below 2 K has recently been reported in YFe₂Ge₂ [10,11], although this is an intensively debated material [12,13]. On the other hand, hydrogen substitution has proven to be a particularly interesting route

to induce superconductivity in these systems. Specifically, the carrier doping limit of the original F substitution in LaFeAsO has been surpassed with hydrogen, thus revealing a two-dome superconductivity [14] together with a second magnetic phase in the additional parent compound LaFeAsO_{0.5}H_{0.5} [15]. In this Rapid Communication, we report the synthesis, crystal structure, and physical properties of the novel compound LaFeSiH. In addition, we study the behavior of the system under hydrostatic pressure and perform DFT calculations to obtain the corresponding electronic band structure and magnetic ground state of this compound. Thus, we find that the new compound LaFeSiH is isostructural, isoelectronic, and also “isomagnetic” to the 1111 family of Fe-based SCs. Most importantly, we find superconductivity with onset at 11 K in this pnictide- and chalcogenide-free system.

Crystal structure. We synthesized the silicide hydride LaFeSiH as described in [16], and singled out two micrometric single crystals (s_1 and s_2) from two powder samples (p_1 and p_2). The compound is stable in air, and its room-temperature crystal structure corresponds to the tetragonal space group $P4/nmm$ with the structural parameters shown in Table I. This structure was determined from the Rietveld refinement of the x-ray and neutron powder diffraction pattern and more accurately from single-crystal x-ray diffraction measurements (see Fig. 1 and [16]). Compared to LaFeSi [17], the new compound displays a variation of the lattice parameters that is highly anisotropic: $a = 4.098 \rightarrow 4.027$ Å and $c = 7.133 \rightarrow 8.014$ Å. This variation is due to the hydrogen insertion at the $2b$ Wyckoff position, as observed in other CeFeSi-type hydrogenated intermetallics [18]. This insertion is confirmed from both the single-crystal x-ray diffraction pattern and the neutron diffraction data that, in addition, reveals the full occupancy of the H atoms at the $\text{HLa}_{4/4}$ tetrahedra (see Fig. 1 and [16]) thus confirming the LaFeSiH stoichiometry. Additionally, we performed DFT calculations that reveal that this is a very stable position for the H atom. Specifically, the overall $P4/nmm$ structure is found to have a well-defined phonon

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TABLE I. Structure parameters of LaFeSiH. 293 K: The atomic positions were obtained from single-crystal x-ray diffraction (*s1*) using JANA2006 [20] and the cell parameters from the powder. The high quality of the single crystal enables the identification of the $2b$ H-atom position already from its x-ray diffraction pattern (see Fig. 1). This is further confirmed from the neutron powder diffraction data using the FULLPROF SUITE program [21] (see [16]). 15 K: Structure parameters obtained from Rietveld refinements of x-ray synchrotron powder data (*p1*) using the DIPTAS software [22].

293 K— $P4/nmm$ (No. 129, origin 2)				
$a = 4.0270(1) \text{ \AA}, c = 8.0374(8) \text{ \AA}$				
	Wyckoff pos.	x	y	z
La	$2c$	$1/4$	$1/4$	$0.6722(1)$
Fe	$2a$	$3/4$	$1/4$	0
Si	$2c$	$1/4$	$1/4$	$0.1500(5)$
H	$2b$	$3/4$	$1/4$	$1/2$
15 K— $Cmme$ (No. 67)				
$a = 5.6831(6) \text{ \AA}, b = 5.7039(6) \text{ \AA}, c = 7.9728(6) \text{ \AA}$				
	Wyckoff pos.	x	y	z
La	$4g$	0	$1/4$	$0.1747(3)$
Fe	$4b$	$1/4$	0	0
Si	$4g$	0	$1/4$	$0.655(1)$
H	$4a$	$1/4$	0	0

spectrum with H-related optical phonons of frequencies greater than 100.5 meV (see also [19]). Thus, we conclude that the room-temperature crystal structure of LaFeSiH is essentially the same structure of the 1111 Fe-based SCs (e.g., LaFeAsO) as illustrated in Fig. 1.

We also determined the low-temperature crystal structure by performing additional x-ray synchrotron experiments at 15 K. The refinement of the corresponding structure revealed a low-temperature phase of LaFeSiH with space group symmetry $Cmme$. The structural parameters of this phase are in Table I. The orthorhombic distortion is rather small, which is again similar to that observed in Fe-based SCs.

Electronic and magnetic structure. We first computed the electronic structure of LaFeSiH assuming a nonmagnetic ground state using the WIEN2K code [23] (see [16] for details). We took the experimental low-temperature structural parameters as input. However, since the orthorhombic distortion is

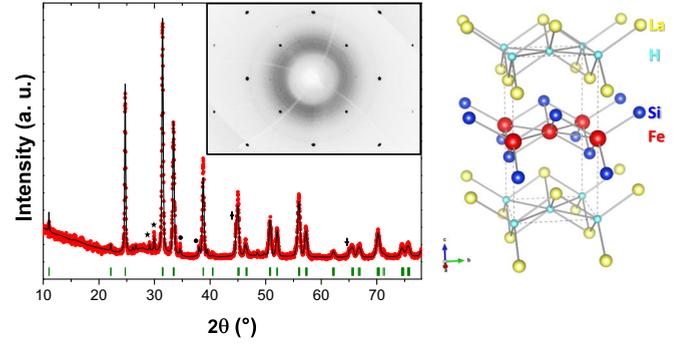


FIG. 1. Left: Room-temperature x-ray powder diffraction pattern of LaFeSiH (*p1*). Ticks indicate the Bragg peaks of the $P4/nmm$ structure of the main LaFeSiH phase while stars, crosses, and circles indicate extra peaks due to the secondary phases La_2O_3 , $\alpha\text{-Fe}$, and $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_x$, respectively, that could not be completely eliminated by annealing. The ($hk0$) plane of the LaFeSiH single-crystal diffraction pattern at room temperature is shown in the inset (*s1*). Right: Ball-and-stick model of the crystal structure of LaFeSiH.

very small, we averaged the a and b parameters and considered an effective tetragonal structure. In Fig. 2(a) we show the calculated electronic density of states (DOS) and the partial DOS (PDOS) projected on the Fe $3d$ orbitals. As we can see, the system has a metallic nature with a DOS at the Fermi level that is largely dominated by the Fe $3d$ orbitals. The corresponding band structure is shown in Fig. 2(a), where the size of the symbols reflects the PDOS of the $3(d_{xz} + d_{yz})$ Fe orbitals. This structure reveals the presence of several bands crossing the Fermi energy, which renders the system a multiband character. Specifically, we have two hole bands centered at the Γ point and two additional bands around the M point. In addition, there is a third band centered at the Γ point below the Fermi energy but very close. The resulting Fermi surface is shown in Figs. 2(b) and 2(c). This Fermi surface has a resemblance to the characteristic Fermi surface of the Fe-based SCs. The central lobe originating from the outer hole band and the belly of the otherwise cylindrical electron sheets represent the main differences.

The nesting properties of the LaFeSiH Fermi surface are limited compared to most of the Fe-based SCs. Yet this system can develop some type of magnetic order. Thus, we performed additional DFT calculations in which different magnetic states

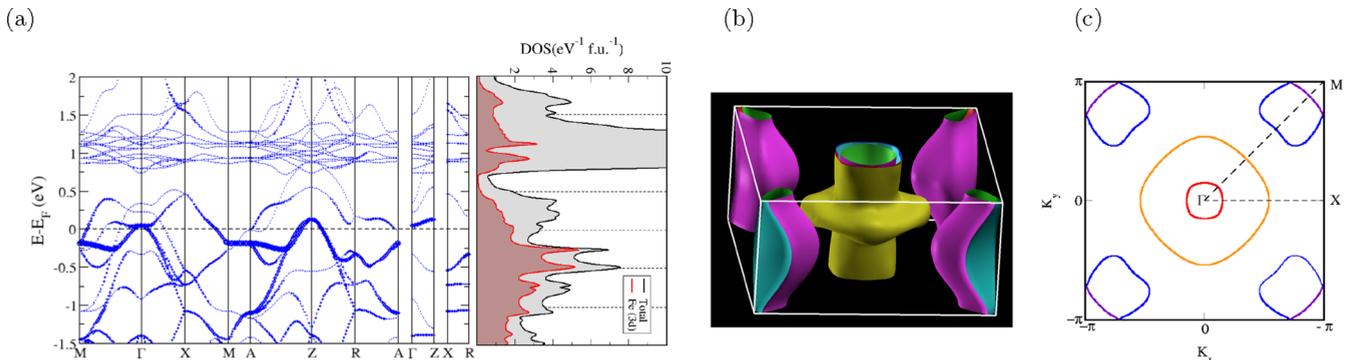


FIG. 2. (a) Band structure and total DOS and PDOS of the Fe- $3d$ states. (b) Three-dimensional view of the Fermi surface and (c) cross section in the $k_z = 0$ plane.

TABLE II. Energy difference with respect to the nonmagnetic state and Fe magnetic moments for various magnetic configurations obtained from DFT calculations. The lowest energy is indicated in bold.

	Checkerboard	FM	Double stripe	Single stripe
ΔE (meV/Fe)	-5.71	-11.11	-11.26	-44.56
μ_{Fe} (μ_{B})	0.90	0.65	1.04	1.16

were considered within the local density (LDA) [24] and the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [25]. Specifically, we studied the tendency of the nonmagnetic tetragonal structure toward ferromagnetic (FM), single-stripe AFM, double-stripe AFM, and checkerboard AFM ordering of the Fe spins. The energy differences with respect to the nonmagnetic state and the corresponding magnetic moments are reported in Table II. We find that the single-stripe AFM order reduces considerably the total energy of the system, and therefore is expected to be the ground state of the system. This explains the orthorhombic distortion we observed experimentally, as this is expected to be a by-product of the single-stripe AFM order triggered by magnetostructural coupling [3,4,26].

Crystal and magnetic structure under pressure. Next, we study the orthorhombic low-temperature structure of the system under external pressure. In Fig. 3 we show the evolution of the orthorhombic distortion at 15 K obtained from our x-ray synchrotron measurements on $p1$. We find that this distortion is suppressed by the application of external pressure and eventually disappears at $P_{c1} \simeq 9.4$ GPa. This is similar to the observed in most of the Fe-based SCs. Interestingly, by further increasing the pressure the structural distortion reemerges at $P_{c2} \simeq 12.7$ GPa. This behavior strongly resembles the observed in LaFeAsO by means of H doping [15].

In order to elucidate the nature of the high-pressure state we performed additional DFT calculations as a function of pressure for the aforementioned magnetic configurations. In these calculations, the single-stripe AFM state was always found to be the lowest-energy state. In Fig. 4 we show the resulting Fe magnetic moment and the energy difference with respect to the nonmagnetic state as a function of pressure. Although

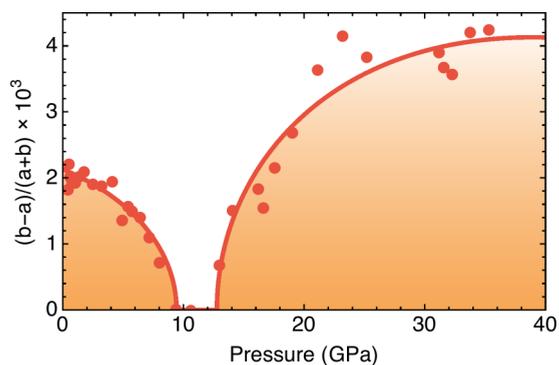


FIG. 3. Relative difference between the a and b lattice parameters of LaFeSiH at 15 K as a function of pressure. Lines are guides to the eye.

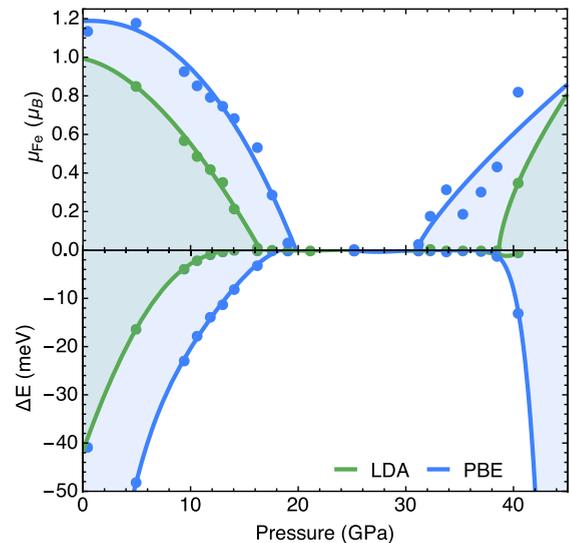


FIG. 4. Calculated Fe magnetic moment in the single-stripe AFM state (top) and energy difference with respect to the nonmagnetic state (bottom) as a function of pressure. The results obtained with LDA and PBE functionals are represented by blue and green points, respectively. Lines are guides to the eye.

the precise numerical values depend on the DFT method, they are in remarkably good agreement with the experimental observations. Namely, the application of external pressure first produces the suppression of single-stripe AFM order which then reemerges as the pressure is further increased. Moreover, according to these results, the reemergence is expected to be discontinuous. The reason is that, even if a nonvanishing Fe magnetic moment is developed, the energy of the single-stripe AFM state requires some extra pressure to eventually become lower than the energy of the nonmagnetic state. The structural distortion observed in our experiments, however, displays rather continuous behavior. Note that this distortion is just a by-product of the magnetic order induced by magnetostructural coupling, and hence is quite small. Consequently, the magnetic discontinuity expected from the DFT calculations could be very difficult to observe indirectly via the lattice distortion. In any case, these calculations are remarkably consistent with the structural behavior observed in our x-ray experiments (see Fig. 3).

Electrical resistivity and magnetization. Figure 5 displays the electrical resistivity measured in LaFeSiH single crystal ($s2$), which reveals the emergence of superconductivity in this novel compound. Specifically, the resistivity shows a T^2 Fermi-liquid behavior before the onset of superconductivity at 11 K (see also Fig. S6 in [16]). From the drop in the resistivity to 50% of its value at the onset we find the superconducting transition temperature $T_c = 9.7$ K at zero field. The inset in Fig. 5 displays the values of the upper critical field H_{c2} determined from the dependence of T_c on the magnetic field applied in the ab plane that can be seen in the main figure. Using these values and the Werthamer-Helfand-Hohenberg formula $H_{c2}(0) = -0.69 T_c dH_{c2}(T)/dT|_{T_c}$, we find $H_{c2}(0) \simeq 17$ T and the zero-temperature correlation length $\xi(0) \equiv \{\Phi_0/[2\pi H_{c2}(0)]\}^{1/2} \simeq 4.3$ nm. Note that the LaFeSiH T_c cannot be explained in terms of conventional electron-phonon

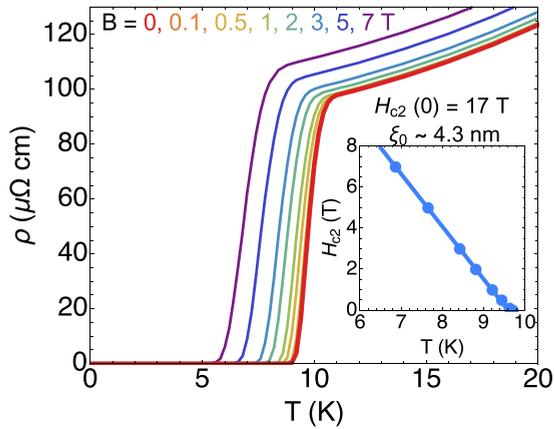


FIG. 5. Low-temperature resistivity as a function of temperature measured in single-crystal LaFeSiH (*s2*) for different values of the magnetic field applied in the *ab* plane. The inset shows the upper critical field as a function of temperature obtained from this data.

mediated superconductivity since it requires an unphysical $\mu^* = 0$ Coulomb pseudopotential [19].

In addition, we used the powder sample *p1* to determine the onset of superconductivity as a function of pressure from similar measurements [see Fig. S5(b) in [16]]. We find that pressure suppresses this onset in a rather smooth fashion as can be seen in Fig. 6. This behavior has a resemblance to that observed for the orthorhombic distortion (see Fig. 3), and hence suggests a strong interplay between the corresponding instabilities. The reemergence observed in the orthorhombic distortion, however, is not observed for the superconductivity below 21 GPa.

Figure 7(a) shows the magnetization as a function of the external field measured in the powder *p1*. The initial magnetization is due to the presence of the secondary ferromagnetic phases α -Fe and $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_x$ and depends on the history of the sample. However, we note that the slope of the curve is negative and can be as strong as $dM/dH \sim -0.18$. This implies a global diamagnetic response whose strength is 4.4×10^2 higher than that of pyrolytic carbon. This gives a lower-bound value for the superconducting diamagnetic strength of LaFeSiH, since it contains the sizable contribution of the aforementioned ferromagnetic phases. For the same

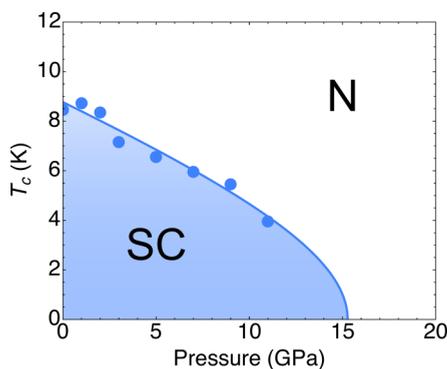


FIG. 6. Superconducting onset as a function of pressure obtained from the resistance of the powder *p1*.

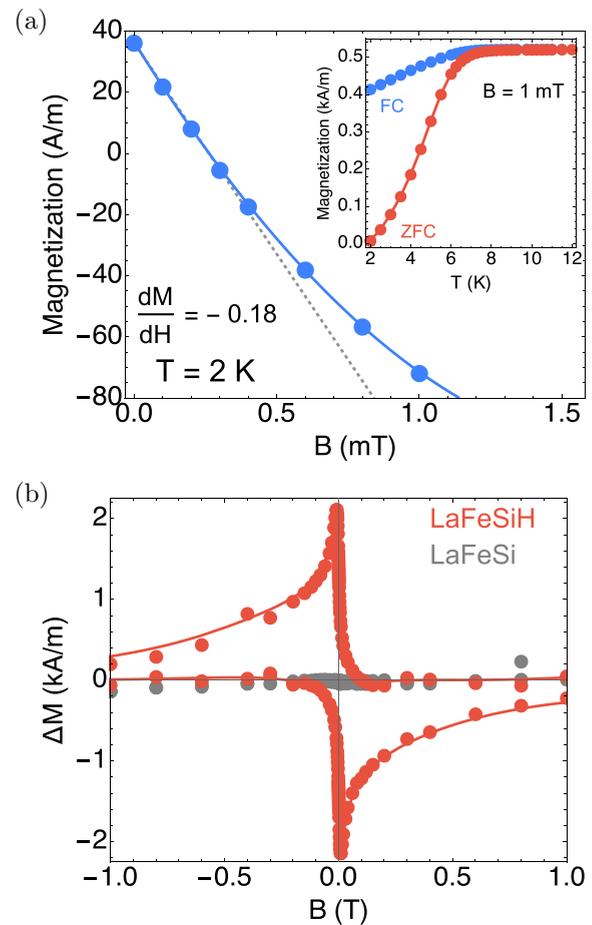


FIG. 7. (a) Magnetization as a function of the external field at 2 K in *p1*. The diamagnetic response $dM/dH = -0.18$ evidences superconductivity in LaFeSiH. Inset: magnetization as a function of temperature at $B = 1$ mT in *p2*, revealing an $\sim 64\%$ superconductor volume fraction in this powder sample. (b) Superconducting hysteresis loop obtained from the magnetization loop at 2 K (below T_c) by subtracting by the loop at 10 K (above T_c) (*p2*). The gray points correspond to the same subtraction for the nonhydrogenated original LaFeSi powder, which contains the same secondary ferromagnetic phases but is not a superconductor (and hence displays no hysteresis).

reason, the value $H_{c1} \sim 0.3$ mT that can be deduced for the lower critical field from the change in the slope has to be taken as a lower-bound value. The inset in Fig. 7(a) shows the magnetization as a function of temperature measured in the powder *p2* (see [16] for additional data in *p1*). The change observed in the zero-field-cooled (ZFC) curve between 10 and 2 K reveals a superconductor volume fraction of $\sim 64\%$ in this powder.

We note that the ferromagnetic signal in our powders sets in at a much higher temperature [$T_{\text{FM}} = 1044$ K for α -Fe [27] and 233–336 K for $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_x$ [28]] and therefore is essentially temperature independent in the low-temperature regime (see Fig. S4 in [16]). Thus, by subtracting the magnetic loop obtained at 10 K from the one at 2 K we can obtain the remaining contribution due to the superconducting LaFeSiH. The resulting hysteresis loop is shown in Fig. 7(b).

Conclusions. We have introduced FeSi as a building block for iron-based superconductivity, which inaugurates a supplementary track to understanding the rich physics of high-temperature superconductors. We have reported the synthesis of the novel silicide hydride LaFeSiH displaying superconductivity with onset 11 K. In addition, this silicide hydride displays structural, magnetic, and electronic features similar to previously reported iron-based superconductors; namely, a low-temperature tetragonal-to-orthorhombic distortion likely related to antiferromagnetic order and a multiband quasi-2D Fermi surface largely dominated by Fe-3d orbitals. LaFeSiH therefore demonstrates the possibility of iron-based superconductivity in a pnictogen- and chalcogen-free fashion. Thus, beyond its fundamental significance from both chemistry and physics points of

view, LaFeSiH is expected to stimulate further research toward practical applications of iron-based superconducting materials.

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