PHYSICAL REVIEW B **78**, 060505(R) (2008)

LiFeAs: An intrinsic FeAs-based superconductor with $T_c = 18$ K

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(Received 23 July 2008; published 18 August 2008)

The synthesis and properties of LiFeAs, a high-T_c Fe-based superconducting stoichiometric compound, are reported. Single crystal x-ray studies reveal that it crystallizes in the tetragonal PbFCl type (P4/nmm) with $a = 3.7914(7)$ Å and $c = 6.364(2)$ Å. Unlike the known isoelectronic undoped intrinsic FeAs compounds, LiFeAs does not show any spin-density wave behavior but exhibits superconductivity at ambient pressures without chemical doping. It exhibits a respectable transition temperature of $T_c = 18$ K with electronlike carriers and a very high critical field, $H_{c2}(0) > 80$ T. LiFeAs appears to be the chemical equivalent of the infinite layered compound of the high-T_c cuprates.

DOI: 10.1103/PhysRevB.78.060505 PACS number(s): 74.70.Dd, 61.66.Fn, 74.25.Fy

Until recently the chemical realm of high-T_c superconductivity had been limited mainly to copper oxide-based layered perovskites. The latest search for noncuprate superconductors in strongly correlated electron layered systems has led to the discovery of high-T_c superconductivity in doped quaternary rare-earth iron oxypnictides, ROFePn (R = rare-earth metal and Pn = pnicogen).[1–3] These superconductors generated enormous interest in the materials community due to the high T_c's involved (up to 41–55 K) as well as the critical presence of a magnetic component, Fe, considered antithetical to conventional s-wave superconductivity.[3,4] High-pressure studies suggest maximum T_c in R(O,F)FeAs may be about 50 K but higher T_c's (>50 K) may yet be discovered in structurally different compounds that are electronically related to R(O,F)FeAs.[5] Analogous alkaline-earth iron arsenides, $AeFe_2As_2$ (Ae = Sr and Ba), reportedly having formal $(Fe_2As_2)^{2-}$ layers as in ROFFeAs but separated by simple Ae layers as in the cuprates, were found to behave similarly.[6,7] The $AeFe_2As_2$ phases become superconducting (maximum $T_c \sim 37$ K) with appropriate substitution of Ae atoms with alkali metals.[8,9] It was also found that isostructural compounds KFe_2As_2 and $CsFe_2As_2$ with formal $(Fe_2As_2)^{1-}$ layers were superconducting, having much lower T_c's of 3.8 and 2.6 K, respectively.[9] Moreover, the evolution from a superconducting state to a spin-density wave (SDW) state by chemical substitution was observed in $K_{1-x}Sr_xFe_2As_2$.[9] Critical to the high-T_c FeAs superconductors is the need to introduce sufficient amounts of charge carriers: with electrons (n type) by F doping (15–20 atm %) or holes (p type) by Sr doping (4–13 atm %) in ROFeAs, and (K/Sr) substitution (40:60 atm %) in $AeFe_2As_2$. These results established the unique role of (Fe_2As_2) layers in high-T_c superconductivity. Since simple elemental K, Cs, (K/Sr), or (Cs/Sr) layers separate the (Fe_2As_2) layers in the AFe_2As_2 superconductors, a Li-based analog, LiFeAs, was investigated. Its crystal structure was previously reported to be of the Cu_2Sb type that features a Fe_2As_2 substructure similar to the known FeAs superconductors.[10] However, the locations of the Li atoms were problematic. Herein we report the synthesis, single-crystal structure determination, and superconducting properties of LiFeAs with $T_c = 18$ K.

LiFeAs was synthesized from high-temperature reactions of high-purity Li (ribbons, 99.99%), Fe (pieces, 99.99%), and As (pieces, 99.99%). Stoichiometric amounts of the starting materials were placed and sealed in welded Nb tubes under Ar. The reaction charges were jacketed within evacuated and sealed quartz containers, and heated at 740 °C for 24 h. The reaction was then slowly cooled to room temperature over 1 day. The polycrystalline samples of LiFeAs are black, exhibit metallic luster, and are sensitive to moist air. All preparative manipulations were carried out in a purified Ar-atmosphere glove box with total O_2 and H_2O levels <0.1 ppm. Elemental analyses on single crystals and polycrystalline samples were carried out using an inductively coupled plasma/mass spectrometer (ICPMS), using both laser ablation and acid dissolution. Results of ICPMS analyses indicate a Li:Fe:As mole ratio of 1.00(3):1.03(2):1.00(1), consistent with a stoichiometric composition of LiFeAs. Phase purity and cell parameters of the polycrystalline samples were investigated by powder x-ray diffraction using a Panalytical X'pert diffractometer. Sufficiently sized shiny single crystals of LiFeAs were also isolated for x-ray diffraction analyses. Single crystal x-ray structure determination was performed using a Siemens SMART diffractometer

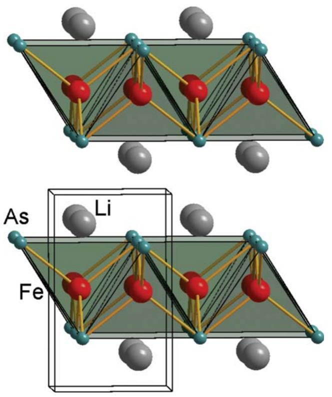

FIG. 1. (Color online) Crystal structure of LiFeAs with Li, Fe, and As shown as large (gray), medium (red), and small (green) spheres, respectively. The unit cell is outlined.

1098-0121/2008/78(6)/060505(4)

TABLE I. Crystal structure parameters of LiFeAs. The equivalent isotropic displacement parameter U(eq) ($\text{Å}^2\times 10^3$) is defined as one third of the trace of the orthogonal U_{ij} tensor. Space group 129, cell choice 2, $a=b=3.7914(7)$ Å, and $c=6.3639(17)$ Å.

Atom	Wyckoff	x	y	Z	U(eq)
As(1)	2c	0.25	0.25	0.2635(1)	8(1)
Fe(2)	2b	0.75	0.25	0.50	7(1)
Li(3)	2c	0.25	0.25	0.8459(15)	21(2)

equipped with a charge coupled device (CCD) area detector. A crystal with dimensions of $0.28\times 0.14\times 0.02$ mm^3 was mounted in glass fiber under a stream of cold nitrogen gas at −58 °C. Monochromatic Mo Ka1 radiation (=0.71073 Å) was used to collect a full hemisphere of data with the narrow-frame method. The data were integrated using the Siemens SAINT program, and the intensities were corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length. Empirical absorption correction was applied using a lamina-shaped model and redundant reflections were averaged. Final unit-cell parameters were refined using 512 reflections having $I > 10\sigma(I)$.

Results of the single-crystal refinement also confirm the conclusions from the chemical analyses. LiFeAs crystallizes in a tetragonal unit cell (P4/nmm) with $a=3.7914(7)$ Å and $c=6.364(2)$ Å. The major structural parameters are summarized in Table I. The crystal structure of LiFeAs, as shown in Fig. 1, is isostructural with the PbFCl type, different from previous reports.[10] It is also different from the superconducting alkali and alkaline-earth metal iron arsenides, $(A/Ae)Fe_2As_2$ (A=K, Rb, and Cs; Ae=Sr and Ba), which crystallize in the $ThCr_2Si_2$ type. However, it is closely related to the "empty" version of LaOFeAs (ZrCuSiAs type). As in LaOFeAs, LiFeAs features Fe_2As_2 layers based on edge-shared tetrahedral $FeAs_4$ units. The Fe_2As_2 layers can also be derived from the alternate As capping of the Fe square nets, above and below each center of the Fe squares. The Fe-As bond distance within the layers is 2.4204(4) Å; the nearest Fe-Fe distance is 2.6809(4) Å. The Fe_2As_2 layers are alternately stacked along the c axis with nominal double layers of Li atoms. The parallel stacking of the FeAs layers in LiFeAs inhibits close interlayer contacts between As atoms. This is different from the "slipped" stacking in $(A,Ae)Fe_2As_2$ wherein adjacent Fe_2As_2 layers are oriented by a mirror plane perpendicular to c passing through $z=1/2$, which allows closer, yet nonbonding, As-As interlayer distances. Although the interlayer distances in LiFeAs [3.182(2) Å] are shorter than the ROFeAs phases, the nearest interlayer As-As distances are long [4.2929(7) Å]. More importantly, unlike LaOFeAs, the nominal tetrahedral sites within the nominal Li-double layers [Li-Li distances of 3.3218(4) Å, as shown in Fig. 1] do not have any notable electron densities and thus are unoccupied.

The results of our structure determination are different from the conclusions of Wang *et al.*,[11] which do not agree with the results of our work in terms of the important aspects of chemical composition of the superconducting phase and the crystal structure. Furthermore, we observed superconductivity in the stoichiometric compound with an elemental ratio Li:Fe:As of 1:1:1 in contrast to the conclusion of Ref. 11, suggesting that a substantial deficiency of Li is needed to induce superconductivity. It is therefore important to verify the real composition that may deviate from the nominal composition if impurity phases form during the synthesis process. The x-ray spectra shown in Fig. 2 do not indicate any impurity phase within the resolution of the measurement.

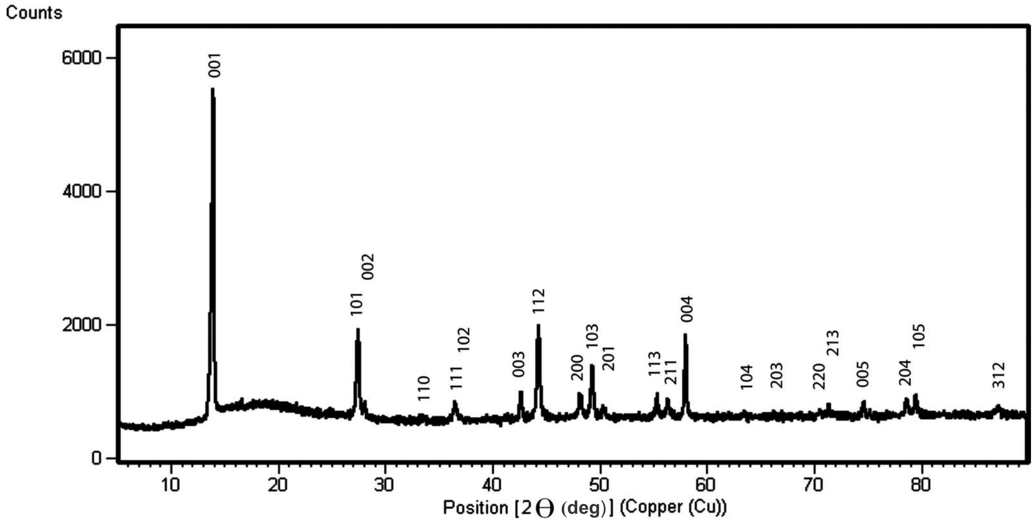

FIG. 2. X-ray powder diffraction of LiFeAs. All peaks can be indexed with the results from the single-crystal refinement. The "hump" around 16°–22° is due to the x-ray scattering of the mylar film used to protect the polycrystalline samples from air.

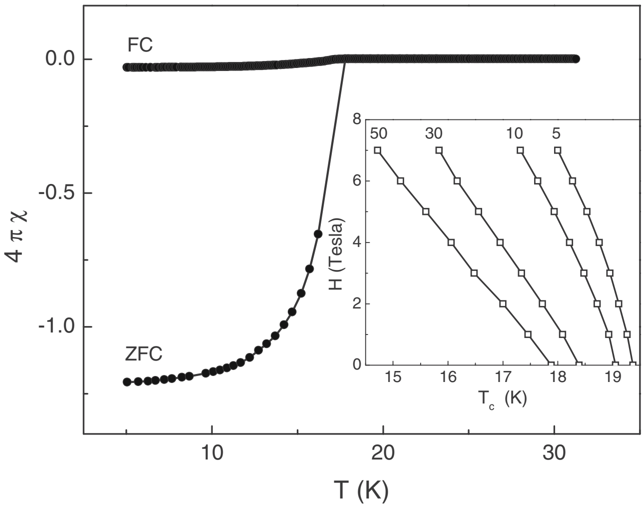

FIG. 3. Magnetic susceptibility of LiFeAs. Inset: Critical fields extracted from the resistivity data (Fig. 4) at different values (percentage labeled) of the resistivity drop.

Furthermore, the ICPMS measurements prove the stoichiometric composition of our sample and its uniformity within the high resolution of the methods used. Our conclusions derived from powder and single-crystal x-ray diffraction experiments are consistent with recent neutron powder-diffraction studies.[12] The slightly lower superconducting T_c of the latter work (T_c=16 K) is possibly due to the off-stoichiometry (slightly Fe-richer) composition of their samples.

Magnetic susceptibility and transport measurements were performed on single phase polycrystalline samples. The powder-diffraction pattern of the sample, as shown in Fig. 2, reveals at least 22 reflections that can be indexed to the P4/nmm space group. No impurity phase can be resolved. Electrical resistivity as a function of temperature $\varrho(T)$ was measured using a standard four-probe method. The magnetic-field effect on ρ was determined using a quantum design physical property measurements system for temperatures down to 1.8 K and magnetic fields up to 7 T. The temperature dependence of the dc-magnetic susceptibility $\chi(T)$ was measured using a quantum design superconducting quantum interference device (SQUID) magnetometer at fields up to 5 T. Thermoelectric power was measured using a low-frequency (0.1 Hz) ac technique with a resolution of 0.02 μV/K. During the measurements, the amplitude of the sinusoidal temperature modulation was kept constant at 0.25 K.

As shown in Fig. 3, LiFeAs exhibits bulk superconductivity as evidenced by a complete diamagnetic shielding signal with a superconductive transition at T_c=18 K. Resistivity measurements ϱ(T) in Fig. 4 also show that LiFeAs is metallic with ϱ decreasing with temperature and features a markedly negative curvature. This negative curvature can be a consequence of strong electron-electron correlation, as in KFe_2As_2, or from strong electron-phonon interaction. The ϱ dramatically drops to almost zero below 18 K. A residual resistance observed below T_c is due to grain-boundary contributions.

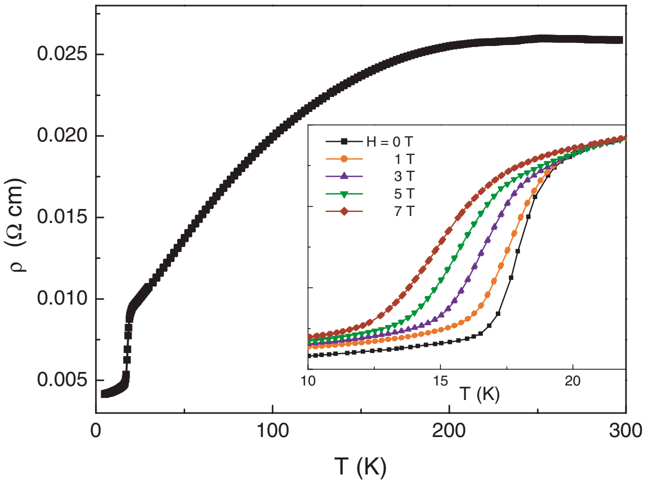

FIG. 4. (Color online) Resistivity of LiFeAs. The inset shows the field dependence near the superconducting transition.

The superconducting transition indicated by the $\varrho(T)$ and $\chi(T)$ plots are consistent with the thermoelectric power $S(T)$ data in Fig. 5. The thermoelectric power, less sensitive to grain boundaries of polycrystalline samples, is zero below T_c within the resolution of the measurement. Also, the large negative thermoelectric power of LiFeAs indicates that its major carriers are electronlike (*n*-type), similar to the *R*(O/F)FeAs superconductors, and are in contrast to the holelike carriers in KFe_2As_2 and (K/Sr)Fe_2As_2.[9] Furthermore, applied magnetic field was observed suppressing the transitions, as expected for superconducting compounds (inset of Fig. 4). The critical-field H vs T_c is shown in the inset of Fig. 3 with T_c defined at resistivity values corresponding to changes of 5%, 10%, 30%, and 50% in the total drop across T_c. Using the Ginzburg-Landau formula for the critical field, $H_c(t)=H_c(0)*(1-t^2)/(1+t^2)$ with $t=T/T_c$, a high zero-temperature critical field (H_{c2}) >80 T can be extrapolated from the data derived from the 5% resistivity drop (Fig. 3).

LiFeAs is isoelectronic with $AeFe_2As_2$ and LnOFeAs in that all have formal $(Fe_2As_2)^{2-}$ layers. In these three compounds, elemental Li-double layers, Sr or Ba layers, or (R_2O_2) slabs separate the charge carrying (Fe_2As_2) layers. This arrangement is similar to the Ae- or *R*-based layers that separate current carrying (CuO_2) layers in high-T_c cuprates.

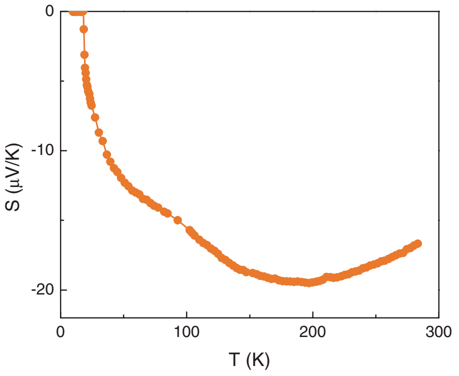

FIG. 5. (Color online) Thermoelectric power of LiFeAs.

Furthermore, undoped parent phases of previously reported iron arsenides are not superconducting at ambient pressures but exhibit magnetic ordering. Spin-density wave transitions are observed in $\mathrm{AeFe_2As_2}$ ($\mathrm{Ae{=}Sr}$ and Ba) (Ref. 7) and LaOFeAs.[1] It is therefore surprising that intrinsic LiFeAs does not appear to show a SDW but exhibits superconductivity with a respectable $T_c = 18$ K. The superconducting behavior of LiFeAs can be roughly explained by assuming incomplete charge transfer from the strongly polarizing Li atoms to the electron-rich $(\mathrm{Fe_2As_2})^{2-}$ layers. However, this would lead to holelike behavior of the carriers, in conflict with the thermoelectric power data. The inconsistency may arise from changes in the conduction bands of the FeAs layers due to variations in interlayer distances. Detailed band-structure calculations as recently reported[13] could help in deepening the insight into the electronic structure and the Fermi surface to understand the complex properties of this class of compounds. High-pressure experiments and varying the electron counts on the $(\mathrm{Fe_2As_2})^{(2\pm x)-}$ layers on the superconducting properties of LiFeAs by chemical doping may help unravel the puzzle. One may also infer that the character of charge carriers (electrons or holes) is related to the stacking arrangement of the $(\mathrm{Fe_2As_2})$ layers. Proper explanation of the puzzling behavior of LiFeAs would significantly help elucidate the mechanism of high-T_c superconductivity in the layered iron pnictides, as well as the layered cuprates. The similarities between the layered FeAs superconductors and the layered cuprate superconductors have been pointed out previously by us and others. Thus, LiFeAs may be equivalent to the infinite layered member of the high-T_c cuprates.

In conclusion, a high-T_c Fe-based superconductor, LiFeAs, with a T_c of 18 K and a very high H_{c2} has been reported, and its structure unambiguously determined. Addition of LiFeAs to the list of structurally different yet isoelectronic FeAs superconductors provides further evidence to the important role of FeAs layers in this class of high-T_c materials. The electron nature of the carriers and superconductivity in undoped LiFeAs raise interesting questions that warrant detailed band-structure calculations and further experiments.

This work was supported by the National Science Foundation (Grant No. CHE-0616805), the R. A. Welch Foundation, the United States Air Force Office of Scientific Research, at Lawrence Berkeley National Laboratory through the United States Department of Energy, and the State of Texas through the Texas Center for Superconductivity. C.W.C. also acknowledges support from the T. L. L. Temple Foundation, and the J. J. and R. Moores Endowment.

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