

A New Pnictide Superconductor without Iron

Jian-Tao Han, Jian-Shi Zhou,* Jin-Guang Cheng, and John B. Goodenough
Texas Materials Institute, ETC 9.102, University of Texas at Austin, Austin, Texas 78712

Received August 13, 2009; E-mail: jszhou@mail.utexas.edu

Soon after the discovery of the new superconductor $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ of the so-called 1111 series, the superconductive transition temperature T_c was optimized from 26 K to ~ 55 K by substituting other rare-earth ions for La^{3+} ; see the review¹ and references therein. Without changing the basic structural unit supporting superconductivity, i.e. the Fe_2X_2 layer, several new systems such as LiFeAs (111),² AFe_2As_2 ($A = \text{Sr}, \text{Ba}$, and partial potassium substitution for these two alkali earths) (122),³ and $\text{FeSe}_{1-\delta}$ (11)⁴ have also been shown to be superconductive. Unlike high- T_c superconductivity in the perovskite-related copper oxides, substitution on iron sites by several other 3d, 4d, and 5d transition metals is not harmful to the superconductive phase in the iron-based pnictides;⁵ chemical substitutions on the iron sites are even necessary to induce superconductivity in the parent compounds of the 122 systems. Superconductivity, however, does not survive if iron is completely replaced in these 122 systems. Here we report superconductivity with $T_c \approx 3.7$ K in a copper-based pnictide LiCu_2P_2 , which has a crystal structure similar to that of (122) AFe_2As_2 . We have also shown superconductivity in another 111 pnictide, LiFeP , with $T_c \approx 4.1$ K. These results support a multiband superconductivity in the pnictides.

High- T_c superconductivity in the copper oxides with a perovskite-related layer structure occurs with either hole or electron doping of the Mott-insulator parent compounds. The Mott physics clearly plays a role. After more than 20 years of research, a fundamental question is still left without an answer: Why does copper remain unique in giving high- T_c superconductivity in these layered perovskite oxides? The iron-based pnictides offer a totally different story. The parent compound is a metal exhibiting a spin density wave (SDW) at T_{SDW} . The electron density of states near the Fermi energy in the parent compound is even reduced upon doping.⁶ Several bands associated with the Fe–As layers cross E_F ,⁷ and superconductivity appears to rely on a peculiar Fermi surface topology that results from this band crossover.⁸ The scenario of multiband superconductivity⁹ became popular at the very beginning because (a) the parent iron-based pnictides have itinerant electrons and (b) the superconductive phase tolerates a wide range of chemical substitutions and is found¹⁰ where subtle structural distortions are achieved either by hydrostatic pressure or by changing the electron concentration. On the other hand, a neutron inelastic scattering study¹¹ has indicated that a Heisenberg-like spin–spin interaction coexists with a Stoner continuum. This latter observation and an SDW in the parent compound suggest that we cannot simply rule out whether fluctuations from localized spins contribute to superconductive pairing. The scenario of spin fluctuations also makes sense since the pnictide superconductors found so far include magnetic ions like Fe and Ni.¹² To resolve this ambiguity, we have looked into the possibility of replacing iron completely by a nonmagnetic metal.

LiCu_2P_2 and LiFeP were initially synthesized some 40 years ago.^{13,14} However, their low-temperature properties have not been characterized. LiCu_2P_2 has the CeAl_2Ga_2 structure with space group

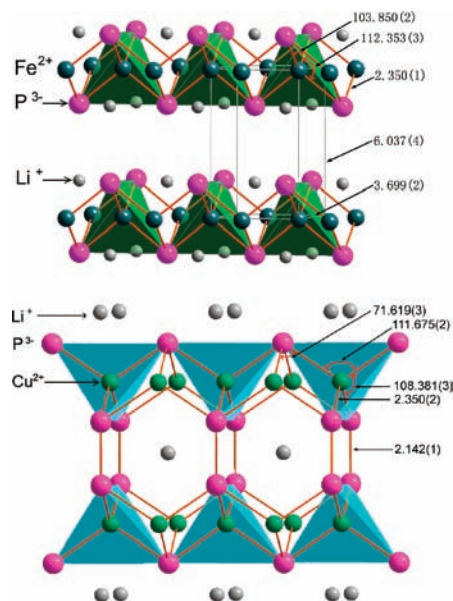


Figure 1. Crystal structures of LiFeP and LiCu_2P_2 . The interatomic distances (Å) and bond angles (degrees) are obtained from the refinement of XRD data at room temperature.

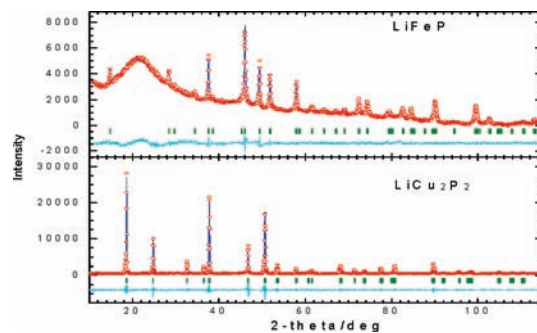


Figure 2. XRD (with $\text{Cu K}\alpha$ radiation) at room temperature and their Rietveld refinements. The data (red open symbol), the profile calculated from refinements (blue line), and their differences (purple line).

$I4/mmm$, whereas LiFeP takes the same structure as that of LiFeAs with the tetragonal space group $P4/nmm$ shown in Figure 1. We synthesized polycrystalline samples of nominal formula LiCu_2P_2 and LiFeP from stoichiometric quantities of high-purity powders of the elements by conventional solid-state reaction. The starting materials were thoroughly ground and pressed into pellets. The pellets were wrapped in Ta foil, sealed in a quartz tube filled with high-purity argon gas, and annealed at 650–850 °C for 24–48 h. All sample manipulations were performed in a glovebox filled with Ar. The product samples were ground into a fine powder for electron energy loss spectroscopy (EELS) and X-ray powder diffraction (XRD) measurements. Results of the EELS show $\text{Li/P} = 0.6 \pm$

0.05 in the final products. The LiCu_2P_2 powder was stable in air, but the gray LiFeP powder was highly air-sensitive, deteriorating within minutes as is also the case for LiFeAs .² Therefore, the LiFeP powder was sealed in the sample holder with amorphous tape inside the glovebox before performing X-ray powder diffraction. The XRD showed a single phase for both samples. Refinements of the XRD patterns (Figure 2) with the Fullprof program gave the lattice parameters $a = 3.8888 \text{ \AA}$ and $c = 9.5620 \text{ \AA}$ for LiCu_2P_2 and $a = 3.6992 \text{ \AA}$ and $c = 6.0374 \text{ \AA}$ for LiFeP as well as important bond lengths and bond angles listed in Figure 1. As in other pnictide superconductors, the face-shared tetrahedra M_2P_2 layer is the common structural unit in both LiCu_2P_2 and LiFeP . It is also worth noting that (a) the Fe–P and Cu–P bond lengths are identical in these two pnictides and (b) the P–Cu (Fe)–P bond angle is close to that found in superconductive AFe_2As_2 ¹⁰ and LiFeAs .²

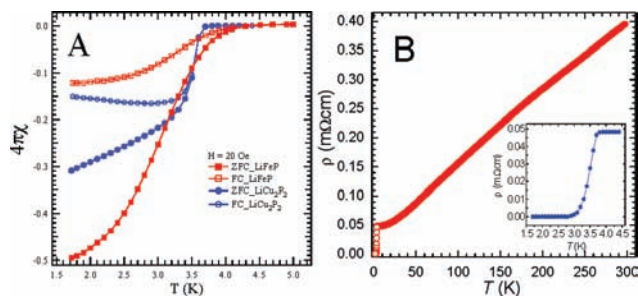


Figure 3. (A) Zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities versus temperature for LiFeP and LiCu_2P_2 measured under a magnetic field of 20 Oe. (B) Temperature dependence of the resistivity of LiCu_2P_2 . The inset shows the detail near T_c .

Magnetic-susceptibility measurements were carried out in a SQUID magnetometer (Quantum Design) under a magnetic field of 20 Oe. Results are shown in Figure 3A. The onset temperature of the Meissner diamagnetic signal is $T_c \approx 3.7$ K for LiCu_2P_2 and $T_c \approx 4.1$ K for LiFeP . The magnitude of the volume susceptibility at 1.7 K indicates an ~ 12 – 15% volume fraction of the superconductive phase in both samples. Superconductivity in LiCu_2P_2 has been further checked by the resistivity drop at T_c in Figure 3B. Figure 3B also shows that the polycrystalline sample has a broad slope change that can be seen near 170 K, which is also commonly observed in all other iron- and nickel-based pnictide superconductors.^{2,3,10,12}

A dramatic slope change of $\rho(T)$ in the parent compounds of iron-based superconductors is caused by a spin density wave forming at T_{SDW} . This dramatic slope change is suppressed in the superconductive phase by either chemical doping or applying hydrostatic pressure. However, a broad transition in $\rho(T)$ at $T > 100$ K which shares some feature of $\rho(T)$ at T_{SDW} remains in the superconductive phase. The close relationship between the broad transition in $\rho(T)$ at high temperatures and superconductivity at low temperatures found in the iron-, nickel-, and now copper-based pnictides signals that the Fermi-surface nesting instability associated with a peculiar Fermi-surface topology in the M_2X_2 layers is the source for the anomalous resistivity and superconductivity. As a matter of fact, superconductivity has been reported in other systems with the ThCr_2Si_2 structure, *viz.*, YbPd_2Ge_2 , LaPd_2Ge_2 , and

LaPt_2Ge_2 ,¹⁵ and recently SrPd_2Ge_2 ,¹⁶ although all with a low T_c . Like the high- T_c copper oxides where superconductivity occurs in the vicinity of a quantum critical point (QCP) as the stripe-ordering phase is suppressed,¹⁸ superconductivity in pnictides is found near a QCP where the SDW phase is suppressed and a structural transition occurs.

The superconductive transition temperature T_c is normally increased by substituting As for P in the superconductive pnictides, e.g. from $T_c = 4$ K in $\text{LaFePO}_{1-x}\text{F}_x$ to 26 K in $\text{LaFeAsO}_{1-x}\text{F}_x$ and from $T_c = 4.1$ K in LiFeP to 18 K in LiFeAs . It would be interesting to check whether superconductivity is formed in a LiCu_2As_2 with the ThCr_2Si_2 structure.

After submitting this communication, we became aware that superconducting LiFeP with $T_c \approx 6$ K has been recently reported by Deng et al.¹⁷

Acknowledgment. This work was supported by the Robert A. Welch Foundation Grant F-1066.

References

- (1) Ishida, K.; Nakai, Y.; Hosono, H. *J. Phys. Soc. Jpn.* **2009**, *78*, 062001.
- (2) (a) Wang, X.-C.; Liu, Q.-Q.; Lv, Y.-X.; Gao, W.-B.; Yang, L.-X.; Yu, R.-C.; Li, F.-Y.; Jin, C.-Q. *Solid State Commun.* **2008**, *148*, 538. (b) Tapp, J.-H.; Tang, Z.-J.; Lv, B.; Sasmal, K.; Lorenz, B.; Chu, Paul C.-W.; Guloy, A.-M. *Phys. Rev. B* **2008**, *78*, 060505. (c) Mito, M.; Pitcher, M.-J.; Crichton, W.; Garbarino, G.; Baker, P.-J.; Blundell, S.-J.; Adamson, P.; Parker, D.-R.; Clarke, S.-J. *J. Am. Chem. Soc.* **2009**, *131*, 2986.
- (3) (a) Rotter, M.; Tegel, M.; Johrendt, D. *Phys. Rev. Lett.* **2008**, *101*, 107006. (b) Sasmal, K.; Lv, B.; Lorenz, B.; Guloy, A.-M.; Chen, F.; Xue, Y.-Y.; Chu, C.-W. *Phys. Rev. Lett.* **2008**, *101*, 107007.
- (4) Hsu, F.-C.; Luo, J.-Y.; Yeh, K.-W.; Chen, T.-K.; Huang, T.-W.; Wu, P.-M.; Lee, Y.-C.; Huang, Y.-L.; Chu, Y.-Y.; Yan, D.-C.; Wu, M.-K. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 14262.
- (5) (a) Saha, S.-R.; Butch, N.-P.; Kirshenbaum, K.; Paglione, J. *Phys. Rev. B* **2009**, *79*, 224519. (b) Ni, N.; Tillman, M.-E.; Yan, J.-Q.; Kracher, A.; Hannahs, S.-T.; Budko, S.-L.; Canfield, P.-C. *Phys. Rev. B* **2008**, *78*, 214515. (c) Ni, N.; Thaler, A.; Kracher, A.; Yan, J.-Q.; Bud'ko, S.-L.; Canfield, P.-C. *Phys. Rev. B* **2009**, *80*, 024511. (d) Han, F.; Zhu, X.-Y.; Cheng, P.; Mu, G.; Jia, Y.; Fang, L.; Wang, Y.-L.; Luo, H.-Q.; Zeng, B.; Shen, B.; Shan, L.; Ren, C.; Wen, H.-H. *Phys. Rev. B* **2009**, *80*, 024506.
- (6) Malaeb, W.; Yoshida, T.; Kataoka, T.; Fujimori, A.; Kubota, M.; Ono, K.; Usui, H.; Kuroki, K.; Arita, R.; Aoki, H.; Kamihara, Y.; Hirano, M.; Hosono, H. *J. Phys. Soc. Jpn.* **2008**, *77*, 69.
- (7) Singh, D. J. *Phys. Rev. B* **2008**, *78*, 094511.
- (8) (a) Sato, T.; Nakayama, K.; Sekiba, Y.; Richard, P.; Xu, Y.-M.; Souma, S.; Takahashi, T.; Chen, G. F.; Luo, J.-L.; Wang, N. L.; Ding, H. *Phys. Rev. Lett.* **2009**, *103*, 047002. (b) Yi, M.; Lu, D.-H.; Analytis, J.-G.; Chu, J.-H.; Mo, S.-K.; He, R.-H.; Moore, R.-G.; Zhou, X.-J.; Chen, G. F.; Luo, J.-L.; Wang, N.-L.; Hussain, Z.; Singh, D.-J.; Fisher, I.-R.; Shen, Z.-X. *Phys. Rev. B* **2009**, *80*, 024515. (c) Terashima, K.; Sekiba, Y.; Bowen, J.-H.; Nakayama, K.; Kawahara, T.; Sato, T.; Richard, P.; Xu, Y.-M.; Li, L.-J.; Cao, G.-H.; Xu, Z.-A.; Ding, H.; Takahashi, T. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 7330.
- (9) Laad, M.-S.; Craco, L. *Phys. Rev. Lett.* **2009**, *103*, 017002.
- (10) Kimber, S.A.-J.; Kreyssig, A.; Zhang, Y.-Z.; Jeschke, H.-O.; Valenti, R.; Yokaichiya, F.; Colambier, E.; Yan, J.; Hansen, T.-C.; Chatterji, T.; McQueeney, R.-J.; Canfield, P.-C.; Goldman, A.-I.; Argyriou, D.-N. *Nat. Mater.* **2009**, *8*, 471.
- (11) Zhao, J.; Adroja, D. T.; Yao, D.-X.; Bewley, R.; Li, S.; Wang, X. F.; Wu, G.; Chen, X. H.; Hu, J.; Dai, P. *Nat. Phys.* **2009**, *5*, 555.
- (12) Watanabe, T.; Yanagi, H.; Kamiya, T.; Kamihara, Y.; Hirano, M.; Hosono, H. *Inorg. Chem.* **2007**, *46*, 7719.
- (13) Schlenger, V. H.; Jacobs, H. *Acta Crystallogr., Sect. B* **1972**, *28*, 327.
- (14) Juza, R.; Langer, K. *Anorg. Allg. Chem.* **1968**, *361*, 58–73.
- (15) Hull, G. W.; Wernick, J.-H.; Geballe, T.-H.; Waszczak, J.-V.; Bernardini, J.-E. *Phys. Rev. B* **1981**, *24*, 6715.
- (16) Fujii, H.; Sato, A. *Phys. Rev. B* **2009**, *79*, 224522.
- (17) Deng, Z. *Europhys. Lett.* **2009**, *87*, 37004.
- (18) Daou, R.; Doiron-Leyraud, N.; LeBoeuf, D.; Li, S. Y.; Laliberte, F.; Cyr-Choiniere, O.; Jo, Y. J.; Balicas, L.; Yan, J.-Q.; Zhou, J.-S.; Goodenough, J. B.; Taillefer, L. *Nat. Phys.* **2009**, *5*, 31.

JA906883Q