Structure and superconductivity of LiFeAs†

Michael J. Pitcher,[a] Dinah R. Parker,[a] Paul Adamson,[a] Sebastian J. C. Herkelrath,[a] Andrew T. Boothroyd,[b] Richard M. Ibberson,[c] Michela Brunelli[d] and Simon J. Clarke*[a]

Received (in Cambridge, UK) 30th July 2008, Accepted 29th September 2008
First published as an Advance Article on the web 20th October 2008
DOI: 10.1039/b813153h

Lithium iron arsenide phases with compositions close to LiFeAs exhibit superconductivity at temperatures at least as high as 16 K, demonstrating that superconducting $[FeAs]^-$ anionic layers with the anti-PbO structure type occur in at least three different structure types and with a wide range of As–Fe–As bond angles.

High temperature superconductivity has recently been reported in several compounds containing FeAs anti-PbO-type (*i.e.* antifluorite-type) layers. LaOFeAs with the ZrSiCuAs structure type was found to superconduct when doped with electrons through the substitution of about 10–20% of the oxide ions by fluoride.[1] This resulted in superconductivity below about 26 K, a critical temperature, T_c, only exceeded by layered cuprate superconductors, some fullerides and MgB_2. Enhancement of T_c to 43 K was achieved in this system at high pressure.[2] Substitution of lanthanum in $LaO_{1-x}F_xFeAs$ by heavier and smaller lanthanides[3–5] results in higher T_cs, and it has been shown that electron doping by the introduction of oxygen deficiency leads to T_cs of up to 55 K in $SmO_{1-x}FeAs$.[6] The high T_cs and critical fields exhibited by these superconductors and their proximity to magnetically ordered phases[7] suggest that they are unconventional superconductors whose properties cannot be described within the framework of existing models of superconductivity such as the BCS theory.

$BaFe_2As_2$ with the common $ThCr_2Si_2$ structure type was found to exhibit similar magnetic and structural behaviour to LaOFeAs.[8] The two compounds are formally isoelectronic as far as their FeAs layers are concerned. Reducing the electron count of $BaFe_2As_2$ to form $Ba_{1-x}K_xFe_2As_2$ produced superconductivity below 38 K[9] and similar doping of $SrFe_2As_2$ also produces superconductivity below 38 K.[10] Superconductivity has been induced at high pressure in stoichiometric AFe_2As_2 (A = Ca, Sr, Ba).[11] Here we use a combination of neutron powder diffraction (NPD) and synchrotron X-ray powder diffraction to describe the crystal structure of a new superconductor LiFeAs which represents a third structure type in which superconducting anti-PbO-type FeAs layers occur. We note that this work is complementary to a recent report of a parallel investigation of this compound.[12]

Investigations by Juza and Langer[13] indicated that the composition LiFeAs could not be obtained but that both Fe-rich and Li-rich compositions could be prepared; for metal : arsenic ratios of 2.1 : 1 single phase compositions were reported between the limits $Li_{1.1}FeAs$ and $Li_{0.96}Fe_{1.14}As$. We initially synthesised‡ a sample (sample 1) with composition 'LiFeAs' by the reaction at 800 °C between stoichiometric quantities of elemental lithium and FeAs (previously prepared from the elements) in a tantalum tube sealed by welding under 1 atm of argon gas. According to powder X-ray diffraction (PXRD) measurements, this black sample was composed of a highly air-sensitive ternary Li_xFeAs phase (89.5(5) mol%) with lattice parameters a = 3.775(1) Å and c = 6.358(2) Å, and 10.5(5) mol% FeAs. Magnetometry measurements‡ showed a sharp superconducting transition with T_c = 16 K (Fig. 1) and the shielding volume fraction was estimated to be close to 100%. Subsequently we attempted the synthesis of 3 g of material of composition $Li_{1.1}FeAs$ using a method similar to that described by Juza and Langer[13] in which Li_3As, Fe and FeAs were ground together in the appropriate stoichiometric

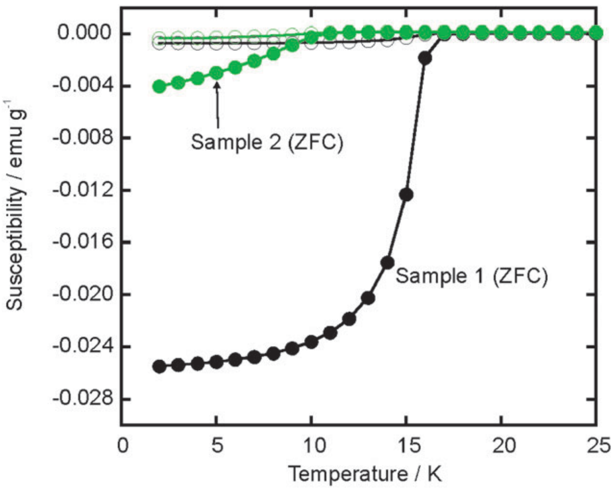

Fig. 1 Magnetic susceptibilities of samples 1 (black symbols) and 2 (green symbols) measured in applied fields of 50 Oe after cooling in zero applied field (ZFC; closed symbols) and after cooling in the measuring field (open symbols).

---

[a] *Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR. E-mail: simon.clarke@chem.ox.ac.uk; Fax: +44 1865 272690; Tel: +44 1865 272600*
[b] *Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, UK OX1 3PU*
[c] *ISIS Facility, STFC-Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, UK OX11 0QX*
[d] *European Synchrotron Radiation Facility, BP, 220, 38043 Grenoble, France*

† Electronic supplementary information (ESI) available: Tables of refined crystallographic parameters and selected bond lengths for samples 1 and 2. See DOI: 10.1039/b813153h

ratio, pressed into a pellet and heated at 800 °C for 48 h in an alumina crucible sealed inside an evacuated silica ampoule. Some attack of the silica tube, presumably by Li, was evident, but the black product (sample 2) appeared single phase according to PXRD measurements with lattice parameters a = 3.774(1) Å and c = 6.354(2) Å, similar, within experimental incertainty, to those of sample 1. Sample 2 exhibited superconductivity below about 10 K, although the shielding volume fraction was much smaller than that of sample 1 and the superconducting transition was less sharp (Fig. 1). We note that both of our samples have lattice parameters equal within experimental uncertainty to those derived from the X-ray powder diffraction pattern in ref. 12 (a = 3.7743(4); c = 6.3551(7) Å using the reported d-spacings). In order to accurately describe the structure sample 2 was measured at 298 K and at 6.5 K on the high resolution time of flight powder neutron diffractometer HRPD at the ISIS facility, UK and on the high resolution powder diffractometer ID31 at the ESRF, France (Fig. 2).‡ Analysis of the NPD data showed unequivocally that the structure was similar to that proposed by Juza and Langer[13] and is composed of an approximately cubic close packed array of As with Fe in half the tetrahedral interstices and Li displaced from the centres of all the octahedral interstices so as to obtain square pyramidal coordination by As. In contrast, in LiMnAs[14] Fe and Li occupy alternate layers of tetrahedral sites in an approximately cubic close packed array of As, thus forming an anti-fluorite superstructure. The location of the lithium ions in LiFeAs is similar to that of half of the Fe ions in Fe_2As (Cu_2Sb type), and the structure of LiFeAs may also be described as the anti-PbFCl type. The refined crystal structure is compared with the crystal structures of Fe_2As and LaOFeAs in Fig. 3. Refinement of the structure at 6.5 K on HRPD indicated no discernable structural distortion, in contrast to the behaviour of non-superconducting LaOFeAs and AFe_2As_2 (A = Sr, Ba). Nor was any magnetic Bragg scattering evident. According to both the ID31 and HRPD refinements sample 2 contained 1.5 mol% of FeAs impurity.

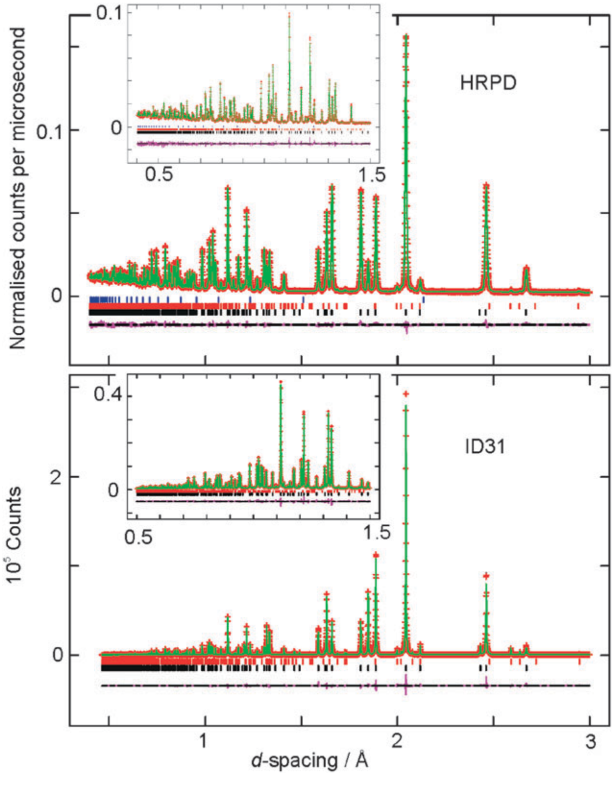

Fig. 2 Results of Rietveld refinement at room temperature against HRPD data (upper: 90 degree bank and 168 degree bank inset) and ID31 data (lower). The data (red points), fit (green line) and difference (lower purple line) are shown. Tick marks indicate reflections for LiFeAs (lowest), FeAs (1.5 mol%; middle) and the vanadium container (uppermost, HRPD data only).

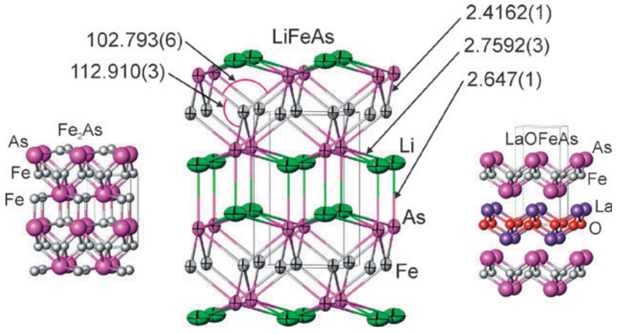

Fig. 3 Comparison of the crystal structures of Fe_2As, LiFeAs, and LaOFeAs. In LiFeAs, lithium ions fully occupy one of the sites which is occupied by Fe in Fe_2As and Li is five-coordinate (square-based pyramid) by As. The interatomic distances (Å) and bond angles (degrees) for LiFeAs are those obtained from refinement against room temperature PND data. 99% anisotropic displacement ellipsoids are shown.

The refinements at room temperature and 6.5 K against PND data both suggested deficiencies of 4–5% on the Li site and 2–3% on the As site. However, the refinement against the ID31 data, which were of higher signal to noise ratio even at d-spacings of 0.6 Å and below, suggested that both sites were fully occupied. A joint refinement with the NPD and Synchrotron PXRD data sets equally weighted yielded a refined composition of $Li_{0.997(4)}FeAs_{0.995(1)}$ where the uncertainties in the fractional occupancies indicate the statistical precision inherent in the refinement,[15] and may underestimate the true uncertainty by up to an order of magnitude. Because of the difference in neutron scattering lengths of Fe (9.54 fm) and Li (−1.90 fm) the apparent 4% deficiency on the Li site suggested from the PND refinements could result from accommodating 0.7% Fe atoms and 99.3% Li atoms on that site, which is chemically plausible given the similar crystal structures of LiFeAs and Fe_2As. The low X-ray scattering amplitude of Li means that even the complementary use of X-rays and neutrons cannot exclude Li/Fe disorder at about the 1% level on the Li site. Juza and Langer[13] suggested that an additional site (3/4,1/4,1/2) carried scattering density corresponding to 10% occupancy by Li. The measurements on HRPD and ID31 both showed that there was much less scattering on this site than their analysis suggested (refined site occupancy factor by Li of 0.011(2) in the joint refinement), and this is consistent with the single crystal X-ray analysis in ref. 12. Chemical analysis‡ on sample 2 produced a composition $Li_{0.83(7)}Fe_{1.0(3)}As_{0.94(3)}$, consistent with the refinement results allowing for the large uncertainty in the determination of the Li content. We conclude from the refinement against powder neutron and synchrotron X-ray data that the main phase in sample 2 is very close to stoichiometric LiFeAs. Analysis of the less pure sample 1 using NPD data from the POLARIS diffractometer at ISIS revealed a structure and composition that was similar within the experimental uncertainty to that for sample 2 determined on HRPD (see ESI‡). The experimental uncertainty in our measurements cannot rule out differences in Li content of up to about 5%.

The originally published structure of LiFeAs[13] is approximate because of the almost negligible X-ray scattering amplitude of lithium. Our analysis using PND data enables accurate location of the lithium ions, which are in sites surrounded by a square pyramid of As atoms (Li–As distances are 2.647(1) Å (×1) and 2.7592(3) Å (×4) at 295 K as shown in Fig. 3). Relative to the Fe atoms, the Li atoms in LiFeAs are in a similar location to the La atoms in LaOFeAs. The structure contains FeAs anti-PbO type layers in common with other recently reported superconductors.[1–11] Our refinement of the structure of sample 2 against PND and synchrotron PXRD data produced an Fe–As distance of 2.4162(1) Å (×4) at 295 K which is similar to the distances of 2.407(2) Å in LaOFeAs[7] and 2.388(3) Å in $SrFe_2As_2$.[16] However the edge-sharing $FeAs_4$ tetrahedra in LiFeAs are compressed in the basal plane relative to the tetrahedra in LaOFeAs and $SrFe_2As_2$: while the As–Fe–As angles in LaOFeAs[7] are 113.7° (×2) and 107.41° (×4) (*i.e.* compressed perpendicular to the basal plane), and the $FeAs_4$ tetrahedra in $SrFe_2As_2$[16] are almost regular (angles of 110.5° (×2) and 108.9° (×4)), the corresponding angles in LiFeAs are 102.793(6)° (×2) and 112.910(3)° (×4) (Fig. 3). Indeed LiFeAs has the smallest basal lattice parameter of all the superconducting iron arsenide phases so far reported and the *occurrence* of superconductivity in compounds containing such layers does not seem highly sensitive to the As–Fe–As bond angles, although the coordination environment is expected to influence the value of T_c. Experiments and computational investigations[17] probing these compounds will shed light on their behaviour.

Our results suggests that other compounds containing FeAs anti-PbO-type layers with Fe in a formal oxidation state close to +2 should be synthesised and their electronic and magnetic properties investigated. Further detailed structural analysis of other phases described by Juza and Langer[13] in the Li–Fe–As system is required to correlate composition and structure with T_c are in progress. The complementary work of Tapp *et al.*[12] describing single crystal X-ray diffraction measurements on stoichiometric LiFeAs with a T_c of 18 K support our conclusions regarding the crystal structure. The superconducting samples of LiFeAs described so far have cell volumes which are very similar even for the range of reported values of T_c between about 10 K and 18 K. The differences in T_c could be due to very small compositional differences[12,13] (*e.g.* <5% differences in Li content) and this is under investigation.

We thank the UK EPSRC for support under grant EP/E025447 and the ISIS facility and the ESRF for the provision of beam time.

Notes and references

‡ Materials: Li rods (Aldrich 99.9%); Fe powder (ALFA, 99.998%), As pieces (ALFA, 99.9999%). FeAs was synthesised by the reaction at 500 °C for four days between ground Fe and As powders in an alumina crucible sealed under vacuum in a silica tube (note that heating to 500 °C was carried out slowly at 0.5 °C min^{-1} to ensure that the As reacted without generating a high vapour pressure). Li_3As was synthesised from Li pieces and As powder in a tantalum ampoule at 500 °C with annealing at 800 °C). Laboratory PXRD data were collected using a PANalytical X'Pert PRO diffractometer operating with $CuK\alpha_1$ radiation in Bragg–Brentano geometry with samples sealed inside air-tight cells. Synchrotron X-ray diffraction data were collected in three hours on about 10 mg of sample 2 sealed inside a 0.7 mm diameter glass capillary tube using the ID31 diffractometer, ESRF, France: $0° \leq 2\theta \leq 55°$, $\lambda = 0.40293(3)$ Å. Time-of-flight NPD data were collected on 3 g of sample 2 and 1.6 g of sample 1 sealed in 6 mm diameter vanadium cylinders using respectively HRPD (30°, 90° and 168° 2θ detectors: $0.3 < d < 7$ Å) and POLARIS (35°, 90° and 145° 2θ detectors: $0.3 < d < 8$ Å) at ISIS, UK: Rietveld analysis was performed using GSAS.[15] Chemical analysis was performed by ICP Atomic Emission Spectroscopy (ITS Testing Services, UK). Magnetic susceptibility (Quantum Design MPMS-XL SQUID magnetometer) measurements were made in a DC field of 50 Oe in the temperature range 2–300 K after cooling in zero applied field and in the measuring field.

Crystal data: LiFeAs (sample 2): joint PND and synchrotron X-ray refinement: $T = 295$ K, tetragonal, space group *P4/nmm* (no. 129), $a = 3.776360(4)$ Å, $c = 6.35679(1)$ Å, $V = 90.6536(2)$ Å^3, $c/a = 1.683$, $Z = 2$; Li (0.25 0.25 0.6536(2); occupancy 0.997(4)), Fe (0.75 0.25 0), As (0.25 0.25 0.23715(3); occupancy 0.995(1)); $wR_p = 0.0521$, $\chi^2 = 10.1$.

1 Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, *J. Am. Chem. Soc.*, 2008, **130**, 3296.
2 H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano and H. Hosono, *Nature*, 2008, **453**, 376.
3 X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang, *Nature*, 2008, **453**, 761.
4 G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo and N. L. Wang, *Phys. Rev. Lett.*, 2008, **100**, 247002.
5 J.-W. G. Bos, G. B. S. Penny, J. A. Rodgers, D. A. Sokolov, A. D. Huxley and J. P. Attfield, *Chem. Commun.*, 2008, 3634.
6 Z. A. Ren, G. C. Che, X.-L. Dong, J. Yang, W. Lu, W. Yi, X.-L. Shen, Z.-C. Li, L.-L. Sun, F. Zhou and Z.-X. Zhao, *Europhys. Lett.*, 2008, **83**, 17002.
7 C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang and P. Dai, *Nature*, 2008, **453**, 899.
8 M. Rotter, M. Tegel, I. Schellenberg, W. Hermes, R. Pöttgen and D. Johrendt, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 020503(R).
9 M. Rotter, M. Tegel and D. Johrendt, *Phys. Rev. Lett.*, 2008, **101**, 107006.
10 G. F. Chen, Z. Li, G. Li, Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang and J. L. Luo, *Chin. Phys. Lett.*, 2008, **25**, 3403; K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y. Xue and P. C. W. Chu, *Phys. Rev. Lett.*, 2008, **101**, 107007.
11 M. S. Torikachvili, S. L. Bud'ko, N. Ni and P. C. Canfield, *Phys. Rev. Lett.*, 2008, **101**, 057006P. L. Alireza, J. Gillett, Y. T. C. Ko, S. E. Sebastian and G. G. Lonzarich, http://arxiv.org/abs/0807.1896v1.
12 J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu and A. M. Guloy, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 060505.
13 R. Juza and K. Langer, *Z. Anorg. Allg. Chem.*, 1968, **361**, 58.
14 W. Bronger, P. Mueller, R. Hoeppner and H. U. Schuster, *Z. Anorg. Allg. Chem.*, 1981, **475**, 9.
15 A. Larson and R. B. von Dreele, *The General Structure Analysis System*, Los Alamos National Laboratory, Los Alamos, NM, 1985.
16 M. Tegel, M. Rotter, V. Weiss, F. M. Schappacher, R. Pöttgen and D. Johrendt, http://arxiv.org/abs/0806.4782v1.
17 D. J. Singh, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 094511.