Structure and superconductivity of LiFeAs
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Lithium iron arsenide phases with compositions close to LiFeAs exhibit superconductivity at temperatures at least as high as 16 K demonstrating that superconducting [FeAs]1−x anionic layers with the anti-PhO 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-PhO-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, Tc, only exceeded by layered cuprate superconductors, some fullerides and MgB2. Enhancement of Tc to 43 K was achieved in this system at high pressure.2 Substitution of lanthanum in LaOxFeAs by heavier and smaller lanthanides3–5 results in higher Tcs and it has been shown that electron doping by the introduction of oxygen deficiency leads to Tcs of up to 55 K in SmOxFeAs.6 The high Tcs and critical fields exhibited by these superconductors and their proximity to magnetically ordered phases7 suggest that they are unconventional superconductors whose properties cannot be described within the framework of existing models of superconductivity such as the BCS theory.

BaFe2As2 with the common ThCr2Si2 structure type was found to exhibit similar magnetic and structural behaviour to LaOFeAs.2 The two compounds are formally isoelectronic as far as their FeAs layers are concerned. Reducing the electron count of BaFe2As2 to form Ba0.75FeAs produced superconductivity below 38 K and similar doping of SrFe2As2 also produces superconductivity below 38 K.10 Superconductivity has been induced at high pressure in stoichiometric AFe2As2 (A = Ca, Sr, Ba).11 Here we describe superconductivity in a sample of almost stoichiometric LiFeAs which represents a third structure type in which superconducting anti-PhO-type FeAs layers occur.

Investigations by Juza and Langer12 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 Li0.6FeAs and Li0.95Fe1.4As. 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 LiFeAs phase (84(1) mol %) with lattice parameters a = 3.775(1) Å and c = 6.358(2) Å, and 16(1) mol % FeAs. Magnetometry measurements (Quantum Design MPMS5) showed a sharp superconducting transition with Tc = 16 K (Figure 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 Li1.25FeAs using a method similar to that described by Juza and Langer12 in which LiAs, Fe and FeAs were ground together in the appropriate stoichiometric ratio, pressed into a pellet and heated at 800 °C for 48 hours 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 very similar to those of Sample 1: a = 3.774(1) Å and c = 6.354(2) Å. Sample 2 exhibited superconductivity below 10 K, although the shielding volume fraction was much smaller than that of Sample 1 and the superconducting transition was slightly less sharp (Figure 1).

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 (Figure 2). Analysis of the data (0.4 < d < 7 Å) using the GSAS suite showed unequivocally that lithium ions were located in square pyramidal positions 5-coordinated by As as proposed by Juza and Langer.12 The structure of the compound is quite different from that obtained for LiMnAs13 in which Fe and Li occupy alternate layers of tetrahedral sites in an approximately cubic close packed array of As. The location of the lithium ions in LiFeAs is similar to that of half of the Fe ions in Fe2As (Cu2Sb type). The refined crystal structure is compared with the crystal structures of Fe2As and LaOFeAs in Figure 3.

Refinement of the structure at 6.5 K indicated no structural distortion, in contrast to the behaviour of non-superconducting LaOFeAs and AFe2As2 (A = Sr, Ba). Nor was any magnetic Bragg scattering evident.

Figure 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).
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. Our refinement of the structure of Sample 2 produced an Fe–As distance of 2.4142(1) Å (× 4) at room temperature which is similar to the distances of 2.407(2) Å in LiFeAs and 2.388(3) Å in SrFe$_2$As$_2$. However the edge-sharing FeAs tetrahedra in LiFeAs are compressed in the basal plane relative to the tetrahedra in LaOFeAs and SrFe$_2$As$_2$; while the As–Fe–As angles in LaOFeAs are 113.7° (× 2) and 107.41° (× 4), the corresponding angles in LiFeAs are 102.870° (× 2) and 112.869° (4) (× 4). 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 $T_c$.

Our results suggest 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 in the Li-Fe-As system is required and correlation of composition and structure with $T_c$ are in progress.

During the preparation of this manuscript we became aware of the work of Jin and co-workers$^{15}$ which reported superconductivity below 18 K in samples containing LiFeAs phases and FeAs as an impurity phase synthesised using high pressure techniques.

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| Atom | Site | x    | y    | z         | $U_{\text{equiv}} / \AA^2 \times 100$ | Refined fractional occupancy |
|------|------|------|------|-----------|-------------------------------------|-----------------------------|
| Fe   | 2a   | 0.75 | 0.25 | 0         | 0.66(1) 0.18(1)                     | 1 1                          |
| Li   | 2c   | 0.25 | 0.25 | 0.6538(1) | 1.61(5) 0.77(6)                     | 0.963(4) 0.950(4)           |
| As   | 2c   | 0.25 | 0.25 | 0.23685(4)| 0.62(2) 0.12(1)                     | 0.972(1) 0.976(1)           |

**Table 1.** Summary of refined parameters for Sample 2 against powder neutron diffraction data

| Atom | $U_{11} = U_{22} / \AA^2 \times 100$ | $U_{33} / \AA^2 \times 100$ |
|------|-------------------------------------|-----------------------------|
| Fe   | 0.580(8)                            | 0.82(1)                     |
|      | 0.184(7)                            | 0.177(9)                    |
| Li   | 1.95(4)                             | 0.94(6)                     |
|      | 0.90(4)                             | 0.50(6)                     |
| As   | 0.535(9)                            | 0.80(2)                     |
|      | 0.089(9)                            | 0.18(1)                     |

**Table 2.** Refined atomic parameters at 298 K (upper) and 6.5 K (lower)

| Instrument | HRPD |
|------------|------|
| Temperature / K | 298 | 6.5 |
| Space group | $P4/nmm$ (No. 129) |
| $a / \AA$ | 3.77543(3) | 3.76982(4) |
| $c / \AA$ | 6.35345(6) | 6.30693(7) |
| $V / \AA^3$ | 90.561(1) | 89.631(2) |
| $R_{wp}$ | 0.0389 | 0.0304 |
| $\chi^2$ | 7.035 | 8.115 |

**Table 3.** Refined anisotropic displacement ellipsoids at 298 K (upper) and 6.5 K (lower)
