

Structure and superconductivity of the layered iron arsenide NaFeAs†

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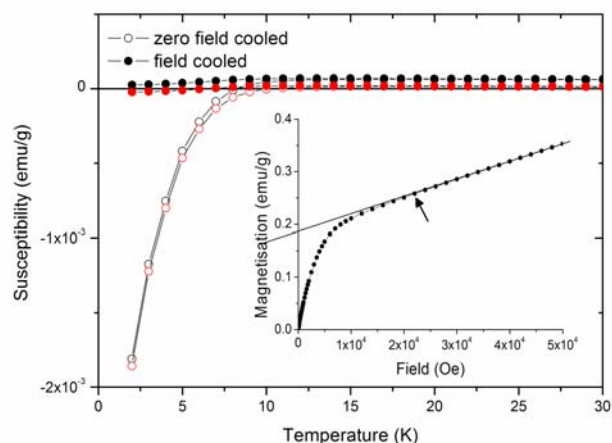
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5 A new iron arsenide superconductor NaFeAs ($T_c = 9$ K) is reported, isostructural with the superconducting lithium analogue, but containing almost regular FeAs₄ tetrahedra similar to those in analogous compounds with the highest critical temperatures.

10 Following the recent discovery that fluorine doped LaFeAsO is a high temperature superconductor ($T_c = 26$ K)¹, a growing class of superconductor has come to light, mainly consisting of compounds containing iron arsenide or iron selenide layers. LaFeAsO takes the ZrSiCuAs structure (filled PbFCl type) and contains anti-PbO or antiferrotype-type FeAs layers in which Fe is tetrahedrally coordinated by As ions. Substituting La for other rare earth metals and electron doping by introducing fluoride or by creating an O-deficiency was found to enhance T_c ,¹⁻⁷ the highest so far being 55 K in SmFeAsO_{1- δ} ,⁵ LaNiPO⁸ and derivatives of LaFePO⁹ with the same structure as LaFeAsO, are also superconducting although with much lower T_c (< 10 K). Superconductivity has also been found in another group of compounds containing FeAs layers: A Fe₂As₂ (where A is an alkaline earth metal) with the ThCr₂Si₂ structure.¹⁰ Hole-doping by partial substitution of A with alkali metals leads to superconductivity with, for example, $T_c = 38$ K in BaFe₂As₂ and SrFe₂As₂.¹¹⁻¹³ At ambient pressure A Fe₂As₂ do not superconduct, however superconductivity can be induced under hydrostatic pressure.¹⁴ Recently, we and others identified LiFeAs, with the PbFCl structure type and containing anti-PbO-type FeAs layers, as a superconductor below 18 K.^{15, 16} As yet, the mechanism for superconductivity in these Fe-As layer based compounds is unclear. Like the high T_c layered cuprate superconductors, the iron arsenide systems seem to be non-BCS superconductors. Current research in the field is generated towards investigating correlations between the occurrence of superconductivity, T_c , electron count and geometric parameters (such as Fe-As bond lengths and As-Fe-As bond angles) by making substitutions at various crystallographic sites. Here we report a new compound, NaFeAs which is isostructural with LiFeAs and is superconducting below 9 K.

NaFeAs was synthesised† by the reaction of stoichiometric quantities of elemental Na, Fe and As. Fe and As powders were ground together and added to pieces of Na in a tantalum tube which was then sealed by welding under 1 atm argon gas; the mixture was heated to 800 °C for 2 days. Preliminary characterisation of the resulting product by powder X-ray diffraction revealed apparently phase pure NaFeAs, isostructural with LiFeAs.^{15, 16}

Fig. 1 shows the magnetic susceptibility versus temperature of NaFeAs measured in an applied field of 50 Oe. Superconducting behaviour is observed below $T_c \approx 9$ K. We



55 **Fig. 1** Zero field cooled (black open circles) and field cooled (black closed circles) susceptibility versus temperature of NaFeAs measured in an applied field of 50 Oe (red open and closed circles show the zfc and fc curves corrected for a Fe impurity of ~0.08% by mass); Inset:

60 Magnetisation versus applied field of NaFeAs, measured at 300 K.

note that, as observed in some samples of LiFeAs,¹⁵ the transition to a superconducting regime appears rather broad. From a rough estimate (without taking a demagnetisation correction into account) the value of the zero-field-cooled susceptibility at 2 K appears much less than that expected for a 100 % superconducting volume fraction. The deviation from a linear plot of magnetisation versus applied field, measured at 300 K, (Fig. 1, inset) indicates the presence of a ferromagnetic impurity in the sample. From an estimate of the saturation field of this impurity we conclude that there is some metallic Fe present in the sample ($H_{\text{sat(Fe)}} \approx 2.2 \times 10^4$ Oe). Given that the saturation magnetisation of Fe is 222 emu/g we calculate the Fe impurity to be approximately 0.08 % by mass, smaller than can reasonably be detected by diffraction methods. The presence of the Fe impurity displaces the susceptibility versus temperature curve in a positive direction; correcting for this impurity (see Fig. 1, red symbols) now reveals a diamagnetic field-cooled susceptibility at low temperature.

80 Structural analysis was carried out by neutron powder diffraction (NPD) using the POLARIS time of flight instrument at the ISIS facility, UK. Fig. 2 shows the Rietveld refinement against data measured at room temperature; the corresponding crystallographic parameters are included in the supplementary information†. Refinement of fractional site occupancies did not indicate any deviation from the stoichiometry NaFeAs which was significant compared with the uncertainty in the refined parameters.

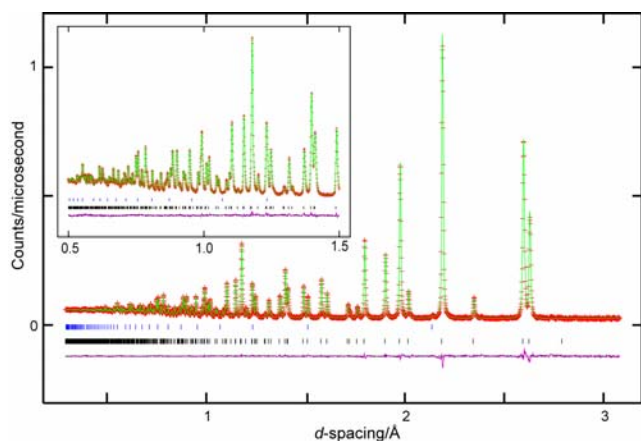


Fig. 2 Results of Rietveld refinement of room temperature POLARIS data (145 degree bank). The data (red points), fit (green line) and difference (purple line) are shown. Tick marks indicate reflections for NaFeAs (black) and the vanadium container (blue); Inset: detail of the region 0.5 to 1.5 Å.

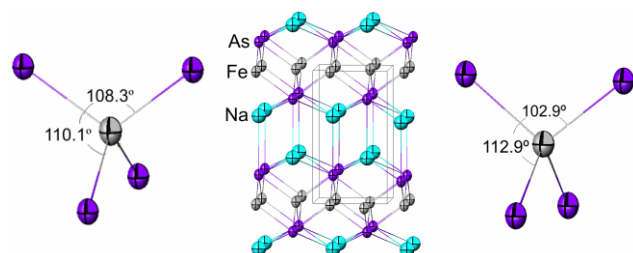


Fig. 3 Centre: Crystal structure of $X\text{FeAs}$ ($X = \text{Li}, \text{Na}$). Fe is tetrahedrally coordinated by 4 As ions; Na (Li) lies in a 5 coordinate square-based pyramidal site between the FeAs layers. Left: Bond angles in the FeAs_4 tetrahedra of NaFeAs (see Table 1). Right: Bond angles in the FeAs_4 tetrahedra of LiFeAs from [15]. 99 % anisotropic displacement ellipsoids are shown.

The crystal structure is similar to that of LiFeAs in which the Fe and As are ions arranged in anti-PbO-type layers (see Fig. 3) with Na ions between the layers in a square-based pyramidal coordination with As. The structure is isotopic with that of PbFCl and is similar to the Cu_2Sb structure which is also adopted by Fe_2As . In the anti-PbO-type layers, the As ions form a distorted tetrahedral arrangement around the Fe ions, giving rise to two distinct As–Fe–As bond angles which we will refer to as α and β (see Fig. 3), according to the notation used in ref. 3. α refers to the As–Fe–As angle formed by two As ions lying above the Fe plane, and β refers to the As–Fe–As angle formed by one As ion lying above and one As ion lying below the Fe plane. In other words, α corresponds to the As–Fe–As bond angle with a multiplicity of 2 and β to the As–Fe–As bond angle with a multiplicity of 4. The values of α and β and the Fe–As bond length are given in Table 1 for LiFeAs and NaFeAs. In LiFeAs, which superconducts below 18 K, α and β are 102.9° ($\times 2$) and 112.9° ($\times 4$) respectively at room temperature giving a tetrahedron which is the most compressed in the basal plane of that of any of the iron arsenide superconductors. In NaFeAs the tetrahedron is almost regular with α and β equal to 108.2° ($\times 2$) and 110.1° ($\times 4$) respectively and the angles are closer to the values observed in the layered iron arsenides which show the highest values of T_c when their electron count is optimised. The NPD pattern was also measured on POLARIS at 2.5 K,

below the superconducting transition at 9 K \ddagger ; no magnetic Bragg peaks were observed at this temperature, nor was any structural transition evident. As for LiFeAs, a slight increase in α and decrease in β was observed at low temperature (see Table 1).

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Table 1 As–Fe–As bond angles in NaFeAs and LiFeAs, measured at room temperature and below T_c .

| | α ($^\circ$)* | β ($^\circ$)* | Fe–As bond length (Å) |
|------------------------------|------------------------|-----------------------|-----------------------|
| LiFeAs (295 K) ¹⁵ | 102.88(1) | 112.865(5) | 2.4141(2) |
| LiFeAs (6.5 K) ¹⁵ | 103.30(1) | 112.643(6) | 2.4035(2) |
| NaFeAs (295 K) | 108.27(2) | 110.07(1) | 2.4366(5) |
| NaFeAs (2.5 K) | 108.74(1) | 109.837(6) | 2.4281(2) |

* α and β refer to As–Fe–As bond angles with multiplicities of 2 and 4 respectively.

Various recent experimental studies of superconductors containing FeAs layers have examined the dependence of superconductivity on the distortion of the FeAs_4 tetrahedra.^{3, 17–19} It was found that in LnFeAsO_{1-y} ($\text{Ln} = \text{La}, \text{Nd}$; $0 \leq y \leq 0.17$),³ T_c decreased with increasing deviation from $\alpha = \beta = 109.47^\circ$ (ideal tetrahedron). Comparison of iron pnictide superconductors in their optimum doping region (i.e. with T_c maximised by tuning the electron count) revealed a clear dependence of T_c on α .³ A study of pressure induced superconductivity in CaFe_2As_2 also shows that T_c decreases with increasing distortion of the FeAs_4 tetrahedra in the superconducting “collapsed” tetragonal phase.²⁰ A recent computational study²¹ suggested that the band structure and density of states are highly sensitive to distortion of the tetrahedral coordination of iron by the arsenide ions. To date, LiFeAs^{15, 16} and NaFeAs appear to be the only iron pnictides which superconduct at ambient pressure when Fe is formally in the +2 oxidation state. Given that they are isoelectronic with many non-superconducting phases (e.g. LaFeAsO , BaFe_2As_2) it is clear that T_c is dependent both on electron count and coordination environment. As NaFeAs contains Fe ions in a near-perfect tetrahedral environment, seemingly the optimal crystallographic condition for superconductivity, it is possible that by modifying the electron count by doping T_c can be enhanced.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: [Tables of refined crystallographic parameters and selected bond lengths; Rietveld refinement of 2.5 K NaFeAs NPD pattern].

[‡] Materials: Na lump (BDH 99.9%), Fe powder (ALFA, 99.998 %), As pieces (ALFA, 99.9999 %). Laboratory PXRD data were collected using a PANalytical X³Pert PRO diffractometer operating with $\text{CuK}\alpha_1$ radiation in Bragg-Brentano geometry with samples sealed inside air-tight cells. Time-of-flight PND data were collected on 1.5 g of sample sealed in a 6 mm diameter vanadium cylinder using the POLARIS diffractometer, ISIS, UK: detector banks at 35° , 90° and 145° 2θ ($0.5 < d < 8.15$ Å). Rietveld analysis was performed using the GSAS suite²².

⁹⁰ Crystal data: NaFeAs: NPD refinement: $T = 295$ K, tetragonal, space group $P4/nmm$ (no. 129), $a = 3.9494(2)$ Å, $c = 7.0396(8)$ Å, $V = 109.804(1)$ Å³, $c/a = 1.782$, $Z = 2$; Na (0.25 0.25 0.64602(7)), Fe (0.75

0.25 0), As (0.25 0.25 0.20278(3)); wR_p (35°, 90° and 145° banks combined) = 0.0209, $\chi^2 = 1.523$

NaFeAs: NPD refinement: $T = 2.5$ K, tetragonal, space group $P4/nmm$ (no. 129), $a = 3.94729(2)$ Å, $c = 6.99112(6)$ Å, $V = 108.930(1)$ Å³, $c/a = 1.771$, $Z = 2$; Na (0.25 0.25 0.64673(8)), Fe (0.75 0.25 0), As (0.25 0.25 0.20234(4)); wR_p (35°, 90° and 145° banks combined) = 0.0129, $\chi^2 = 1.598$.

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Superconductivity in the layered iron arsenide NaFeAs

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Electronic Supplementary Information.

Table S1. Summary of refinement of NaFeAs against Powder Neutron Diffraction (PND) data at 295 K, measured on the POLARIS instrument, ISIS facility, UK.

| | |
|--------------------|---------------|
| <i>Space Group</i> | <i>P4/nmm</i> |
| $a / \text{\AA}$ | 3.9494(2) |
| $c / \text{\AA}$ | 7.0396(8) |
| $V / \text{\AA}^3$ | 109.804(1) |
| R_{wp} | 0.0209 |
| χ^2 | 1.523 |

Table S2. Refined atomic parameters for NaFeAs at 295 K, from data measured on the POLARIS instrument, ISIS facility, UK.

| Atom | Site | x | y | z | $U_{\text{equiv}} / \text{\AA}^2 \times 100$ |
|------|------|------|------|------------|--|
| Fe | 2a | 0.75 | 0.25 | 0 | 0.66(1) |
| Na | 2c | 0.25 | 0.25 | 0.64602(7) | 1.31(1) |
| As | 2c | 0.25 | 0.25 | 0.20278(3) | 0.67(1) |

Table S4. Refined anisotropic displacement parameters for NaFeAs from data measured at 295 K on the POLARIS instrument, ISIS facility, UK.

| Atom | $U_{11} = U_{22} / \text{\AA}^2 \times 100$ | $U_{33} / \text{\AA}^2 \times 100$ |
|------|---|------------------------------------|
| Fe | 0.546(5) | 0.899(8) |
| Na | 1.315(9) | 1.317(9) |
| As | 0.577(7) | 0.856(8) |

Table S5. Summary of refinement of NaFeAs against Powder Neutron Diffraction (PND) data at 2.5 K, measured on the POLARIS instrument, ISIS facility, UK.

| | |
|--------------------|---------------|
| <i>Space Group</i> | <i>P4/nmm</i> |
| $a / \text{\AA}$ | 3.94729(2) |
| $c / \text{\AA}$ | 6.99112(6) |
| $V / \text{\AA}^3$ | 108.930(1) |
| R_{wp} | 0.0129 |
| χ^2 | 1.598 |

Table S6. Refined atomic parameters for NaFeAs at 2.5 K, from data measured on the POLARIS instrument, ISIS facility, UK.

| Atom | Site | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{equiv}} / \text{\AA}^2 \times 100$ |
|------|------------|----------|----------|------------|--|
| Fe | 2 <i>a</i> | 0.75 | 0.25 | 0 | 0.19(1) |
| Na | 2 <i>c</i> | 0.25 | 0.25 | 0.64673(8) | 0.54(3) |
| As | 2 <i>c</i> | 0.25 | 0.25 | 0.20234(4) | 0.22(2) |

Table S7. Refined anisotropic displacement parameters for NaFeAs from data measured at 2.5 K on the POLARIS instrument, ISIS facility, UK.

| Atom | $U_{11} = U_{22} / \text{\AA}^2 \times 100$ | $U_{33} / \text{\AA}^2 \times 100$ |
|------|---|------------------------------------|
| Fe | 0.134(4) | 0.317(8) |
| Na | 0.429(9) | 0.753(9) |
| As | 0.184(7) | 0.298(9) |

Table S8. Refined bond lengths (Å) and angles (degrees) for NaFeAs at 295 K and 2.5 K from data measured on the POLARIS instrument, ISIS facility, UK.

| | 295 K | 2.5 K |
|------------------------|-----------|------------|
| Fe–As [4] ^a | 2.4366(5) | 2.4281(2) |
| Na–As [4] | 2.9886(7) | 2.9842(2) |
| Na–As [1] | 3.1203(9) | 3.1063(6) |
| Fe–Fe [4] | 2.7927(7) | 2.79115(3) |
| Na–Fe [4] | 3.1795(7) | 3.1620(5) |
| Na–Na [4] | 3.4678(9) | 3.4633(7) |
| | | |
| As–Fe–As [2] | 108.27(2) | 108.74(1) |
| As–Fe–As [4] | 110.07(1) | 109.837(6) |
| As–Na–As [4] | 82.713(8) | 82.808(8) |
| As–Na–As[4] | 110.86(1) | 110.72(1) |

^a The number in square brackets indicates the number of symmetry equivalent bond lengths and angles

Figure S1. Rietveld refinements for NaFeAs at 2.5 K, measured on the POLARIS instrument, ISIS, UK. 145° bank. (note: peaks at ~ 2.1 Å from vanadium sample holder and cryostat)

