Suppression of the Superconducting Transition in $R$FeAsO$_{1-x}$F$_x$ for $R =$ Tb, Dy, Ho

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A suppression of superconductivity in the late rare earth $R$FeAsO$_{1-x}$F$_x$ materials is reported. The maximum critical temperature ($T_c$) decreases from 51 K for $R =$ Tb to 36 K for HoFeAsO$_{0.9}$F$_{0.1}$, which has been synthesised under 10 GPa pressure. This suppression is driven by a decrease in the Fe-As-Fe angle below an optimum value of 110.6°, as the angle decreases linearly with unit cell volume (V) across the $R$FeAsO$_{1-x}$F$_x$ series. A crossover in electronic structure around this optimum geometry is evidenced by a change in sign of the compositional $dT_c/dV$, from negative values for previously reported large $R$ materials to positive for HoFeAsO$_{0.9}$F$_{0.1}$.

Rare earth ($R$) oxypnictides $R$FeAsO$^1$ were recently discovered to superconduct when doped, with critical temperatures surpassed only by the high-$T_c$ cuprates. Several families of superconducting iron pnictides have subsequently been
discovered.\textsuperscript{2} These all have layered structures containing AsFeAs slabs with Fe tetrahedrally coordinated by As. The main types are the 1111 materials based on $R\text{FeAsO}$ or $M\text{FeAsF}$ ($M = \text{Ca, Sr, Ba}$), the 122 phases $M\text{Fe_2As_2}$, and the 111 $A\text{FeAs}$ ($A = \text{Li, Na}$) family. The related binaries $\text{FeX}$ ($X = \text{Se, Te}$) are also superconducting.

The electron-doped 1111 materials $R\text{FeAsO}_{1-x}\text{F}_x$ and $R\text{FeAsO}_{1-\delta}$ materials remain prominent as they have the highest $T_c$'s, up to 56 K, and allow lattice and doping effects to be investigated through variations of the $R^{3+}$ cation size and the anion composition. A strong lattice effect is evident at the start of the rare earth series, as $T_c$ rises from 26 K for $\text{LaFeAsO}_{1-x}\text{F}_x$ to 43 K under pressure,\textsuperscript{3,4} and to a near-constant maximum 50-56 K in the $R\text{FeAsO}_{1-x}\text{F}_x$ and $R\text{FeAsO}_{1-\delta}$ series for $R = \text{Pr}$ to Gd,\textsuperscript{5,6,7,8,9,10} but whether lattice effects ultimately enhance or suppress superconductivity for the late $R$'s has been unclear. The late rare earth $R\text{FeAsO}_{1-x}\text{F}_x$ materials and the oxygen-deficient $R\text{FeAsO}_{1-\delta}$ superconductors require high pressure synthesis, leading to significant challenges as single phase samples are difficult to prepare, and accurate analyses of cation stoichiometries and O and F contents are difficult. To investigate the effect of the lattice for later $R$ we have synthesised multiple samples of $R\text{FeAsO}_{0.9}\text{F}_{0.1}$ ($R = \text{Tb, Dy, and Ho}$) under varying high pressure conditions. Here we report superconductivity in $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$ for which the maximum $T_c$ of 36 K is markedly lower than in the previous $R$ analogs. This is part of a systematic suppression of superconductivity by the smaller, late $R$ cations. $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$ also shows a reversal in the sign of the compositional $dT_c/dV$ ($V = \text{unit cell volume}$) compared to the early $R$ materials, confirming that the decreasing $R$ size has a significant effect on the bands contributing to the Fermi surface.
Polycrystalline ceramic $R$FeAsO$_{1-x}$F$_x$ samples ($R = \text{Tb}, \text{Dy}, \text{and Ho}$) were synthesised by a high pressure method and investigated by powder X-ray diffraction, magnetization and conductivity measurements.$^{11}$ Initial results for $R$FeAsO$_{1-x}$F$_x$ ($R = \text{Tb}$ and Dy) were published elsewhere.$^{12}$ Both materials were found to be superconducting with maximum $T_c$’s of 46 and 45 K respectively. Little difference in superconducting properties between samples with nominal compositions of $x = 0.1$ and 0.2 were observed, and the $x = 0.2$ materials were generally of lower phase purity, and so the $x = 0.1$ composition was used in subsequent syntheses. The best samples typically contain ~80% by mass of the superconducting phase with residual non-superconducting $R_2O_3$ and $R$As phases also present. The sample purity and superconducting properties are not sensitive to synthesis pressure over a range that moves to higher pressures as $R$ decreases in size; $R = \text{Tb}$ and Dy superconductors were respectively prepared at 7-10 and 8-12 GPa, heating at 1050-1100 °C. Repeated syntheses of TbFeAsO$_{1-x}$F$_x$ gave several samples with higher $T_c$’s than the above value, the highest value is $T_c$ (max) = 51 K (Fig. 1). Further DyFeAsO$_{1-x}$F$_x$ samples did not show higher transitions than before, so we conclude that $T_c$ (max) in this system is 45 K.

Tetragonal HoFeAsO$_{0.9}$F$_{0.1}$ was obtained from reactions at 10 GPa pressure and the properties of six HoFeAsO$_{0.9}$F$_{0.1}$ samples prepared under varying conditions are summarized in Table 1. Crystal structure refinements and phase analysis were carried out by fitting powder X-ray diffraction data (Fig. 2).$^{13}$ Magnetisation measurements demonstrate that all six HoFeAsO$_{1-x}$F$_x$ samples are bulk superconductors with $T_c$’s of 29-36 K (Fig. 3). Resistivities show smooth high temperature evolutions without apparent
spin density wave anomalies. The transitions to the zero resistance state have widths of less than 4 K.

Although all of the samples in Table 1 have the same starting composition, small variations of synthesis pressure and temperature result in a dispersion in x around the nominal 0.1 value for the HoFeAsO$_{1-x}$F$_x$ phase and corresponding variations in superconducting properties. $T_c$ increases to a maximum value, $T_c$(max), at the upper solubility limit of x in $R$FeAsO$_{1-x}$F$_x$ systems, and this is consistent with the observation that the superconducting phases in samples 1, 3 and 4, which are heated at high temperatures or longer times and so are likely to have a slightly lower F content, have lower $T_c$’s (average 32.1 K) than the other three samples, made under nominally identical ‘optimum’ conditions, which have average $T_c$ = 34.8 K. Sample 6 shows the highest $T_c$ = 36.2 K and the lowest proportion of the HoFeAsO$_{1-x}$F$_x$ phase and a correspondingly low diamagnetic volume fraction. This demonstrates that the sample is at the upper limit of the superconducting composition range and so gives a realistic $T_c$(max) for the HoFeAsO$_{1-x}$F$_x$ system.

Although the doping values x for the high pressure $R$FeAsO$_{1-x}$F$_x$ samples are not known precisely, comparing ensembles of samples with similar phase purities made under similar conditions reveals a clear suppression of superconductivity by lattice effects for heavier $R$. For example, all of our TbFeAsO$_{1-x}$F$_x$ superconductors have higher $T_c$’s (five TbFeAsO$_{1-x}$F$_x$ samples, $T_c$ = 45-51 K) than all of the HoFeAsO$_{1-x}$F$_x$ materials (in Table 1). The $T_c$(max) values of 51, 45 and 36 K for $R$FeAsO$_{1-x}$F$_x$ with $R$ = Tb, Dy and Ho, respectively thus represent the trend correctly.
Fig. 4 shows a plot of the maximum critical temperatures, $T_c$ (max), against unit cell volume for many reported $R$FeAsO$_{1-x}$F$_x$ and $R$FeAsO$_{1.5}$ systems and our above materials. $T_c$ (max) rises slowly as cell volume decreases for $R =$ La to Pr and then shows a broad maximum, between $R =$ Pr and Tb in the $R$FeAsO$_{1-x}$F$_x$ materials, before falling rapidly as $R$ changes from Tb to Dy to Ho. This trend is not seen in the reported $R$FeAsO$_{1.5}$ superconductors, where $T_c$ (max) remains approximately constant,$^{14,15}$ apparently because they have larger cell volumes than their $R$FeAsO$_{1-x}$F$_x$ analogs (see Fig. 4).

The size of the $R^{3+}$ cation tunes the electronic properties through variations in the geometry of the FeAs slab. A trend between the As-Fe-As (or equivalent Fe-As-Fe) angle and $T_c$ has been reported for the early $R$ materials.$^{16}$ The upper panel of Fig. 4 shows representative reported values for optimal $R$FeAsO$_{1-x}$F$_x$ superconductors including our $R =$ Tb, Dy, and Ho materials. This demonstrates that the angle decreases monotonically with $R$ size and so does not show a universal correlation with $T_c$ (max). The $T_c$ (max) variation in the $R$FeAsO$_{1-x}$F$_x$ series is described by a simple $\cos(\phi-\phi_0)$ function, shown in Fig. 4, where the value of the As-Fe-As angle corresponding to the global maximum $T_c$, $\phi_{\text{max}} = 110.6^\circ$, is close to the ideal 109.5° value for a regular FeAs$_4$ tetrahedron. All five of the Fe 3d-bands are partially occupied and contribute to the Fermi surface of the iron arsenide superconductors through hybridization with As 4s and 4p states.$^{17}$ Decreasing the tetrahedral angle through 109.5° marks the crossover from tetragonal compression to elongation of the FeAs$_4$ tetrahedra. In a crystal field model, this reverses the splittings of the $t_2$ and $e$ d-orbital sets and so a significant crossover in the real electronic structure is likely to occur near 109.5°.
Evidence for the above crossover also comes from a discovered change in the sign of the compositional dT_c/dV near optimum doping in the RFeAsO_{1-x}F_x systems. The unit cell parameters and volume for the six HoFeAsO_{1-x}F_x samples in Table 1 show a positive correlation with T_c (Fig. 5), in contrast to early R = La and Sm analogs where lattice parameters and volume decrease with increasing T_c. The T_c,V points for near-optimally doped R = La, Sm and Ho RFeAsO_{1-x}F_x superconductors are shown on Fig. 4 together with the derived dT_c/dV values. dT_c/dV for a single RFeAsO_{1-x}F_x system follows the overall trend in dT_c(max)/dV for different R’s, changing from a negative value at large R = La to a small positive slope at R = Ho.

The compositional dT_c/dV for a given RFeAsO_{1-x}F_x system reflects two competing effects of variations in the fluoride content x on the lattice volume. F^- is slightly smaller than O^{2-} so the anion substitution effect gives a negative contribution to the compositional dT_c/dV, independent of R. The concomitant effect of doping electrons into the Fe d-bands tends to expand the lattice (and increase T_c), but the magnitude of this positive dT_c/dV term depends on the nature of the bands at the Fermi surface. The observed shift from negative to positive dT_c/dV as R changes from La to Ho shows that the decreasing size of the R^{3+} cation leads to significant changes in the Fermi surface, with volume-expanding (antibonding) bands more prominent for smaller R. Calculations have confirmed that the electronic structure near the Fermi level is sensitive to such small changes in the As z-coordinate (equivalent to changing the Fe-As-Fe angle). Small changes in the contributions of the d-bands are likely to be particularly important in a multigap scenario for superconductivity, as evidenced in gap measurements of TbFeAsO_{0.9}F_{0.1} and other iron arsenide materials.
In summary, our analysis of multiple samples of $R$FeAsO$_{1-x}$F$_x$ ($R =$ Tb, Dy, and Ho) superconductors demonstrates that the maximum critical temperature falls from 51 K for $R =$ Tb to 36 K for the previously unreported Ho analog. Hence, the effect on the lattice of substituting smaller, late rare earths in the $R$FeAsO$_{1-x}$F$_x$ lattice suppresses superconductivity. This lattice control appears to be through tuning of the interatomic angles in the FeAs layer, with the optimum angle being 110.6°, near the ideal tetrahedral value. The compositional $dT_c/dV$ changes sign around the optimum angle evidencing significant changes in the Fermi surface. It appears difficult to increase the critical temperatures above 56 K in 1111 type iron arsenide materials through tuning lattice effects, although the possibility of higher $T_c$’s in other structure types remains open.

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Table 1: Synthesis conditions (all samples were synthesised at 10 GPa), refined lattice parameters and volume, $T_c$’s, mass fractions and superconducting volume fractions for HoFeAsO$_{1-x}$F$_x$ samples.

| Sample | $t_{\text{synth}}$ (hr) | $T_{\text{synth}}$ (°C) | $a$ (Å)          | $c$ (Å)          | Vol (Å$^3$) | $T_c$ (K) | Mass frac. (%) | Diamag. frac. (%) |
|--------|-----------------|-----------------|-----------------|-----------------|----------|----------|---------------|------------------|
| 1      | 2               | 1150            | 3.8246(3)       | 8.254(1)        | 120.74(3) | 29.3     | 75            | 70               |
| 2      | 2               | 1100            | 3.8272(2)       | 8.2649(8)       | 121.06(2) | 33.0     | 74            | 85               |
| 3      | 1               | 1150            | 3.8258(5)       | 8.264(2)        | 120.96(4) | 33.2     | 73            | 76               |
| 4      | 3               | 1100            | 3.8282(5)       | 8.261(2)        | 121.07(5) | 33.7     | 84            | 74               |
| 5      | 2               | 1100            | 3.8282(2)       | 8.2654(7)       | 121.13(2) | 35.2     | 81            | 57               |
| 6      | 2               | 1100            | 3.8297(7)       | 8.270(2)        | 121.30(7) | 36.2     | 58            | 46               |

Fig. 1 Resistivity and (inset) susceptibility data for an optimum sample of TbFeAsO$_{0.9}$F$_{0.1}$, showing a sharp superconducting transition at $T_c = 51$ K. The sample was prepared at 7 GPa and 1050 °C.
Fig. 2 Fitted x-ray diffraction profile for HoFeAsO$_{0.9}$F$_{0.1}$ (sample 5) at room temperature. The Bragg markers (from top to bottom) are for the minority phases, Ho$_2$O$_3$ and HoAs, and for HoFeAsO$_{0.9}$F$_{0.1}$.

Fig. 3 Superconductivity measurements for HoFeAs$_{0.9}$F$_{0.1}$: (a) ac magnetic volume susceptibility for the six samples; (b) resistivities for samples 4 and 6.
Fig. 4 Variation of Fe-As-Fe angle $\phi$ (upper panel) and superconducting $T_c$ (lower panel) with unit cell volume for different RFeAsO$_{1-x}$F$_x$ (circles)$^{19,22,5,12}$ and RFeAsO$_{1.5}$ (triangles)$^{14,15}$. $T_c$(max) points are shown as filled symbols. The fit of equation $T_c$(max) = $T_c$(max)$_0$.cosA($\phi$-$\phi_0$) with parameters $T_c$(max)$_0$ = 56 K, A = 0.03, and $\phi_0$ = 110.6° is also shown. $dT_c/dV$ values are derived from the data for sub-optimally doped materials (open symbols) in the $R$ = La,$^{19}$ Sm$^7$ and Ho (this paper) systems.

Fig. 5 Variations of $T_c$ with the tetragonal unit cell parameters and volume for the six HoFeAsO$_{1-x}$F$_x$ samples in Table 1.
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Samples were synthesised from stoichiometric amounts of RAs, Fe$_2$O$_3$, FeF$_2$ and Fe, using a Walker multianvil module within a 1000 tonne press. The products were dense, black, sintered polycrystalline pellets. Powder X-ray diffraction data were collected on a Bruker AXS D8 diffractometer using Cu Kα$_1$ radiation. Data were recorded at $10 \leq 2\theta \leq 100^\circ$ with a step size of 0.007$^\circ$ for Rietveld analysis. ac magnetic susceptibility was
measured from 3 to 50 K with a field of 0.5 Oe oscillating at 117 Hz using a Quantum Design SQUID magnetometer. Electrical resistivity was measured by a four-probe method between 1.7 and 300 K using a Quantum Design physical property measurement system and an APD cryogenics closed cycle refrigeration unit with an in-house built sample stage.

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the pressure-induced $dT_c/dV$ at constant $x$. Both derivatives are negative for LaFeAsO$_{1-x}$F$_x$, and we thus predict a positive pressure-induced $dT_c/dV$ (pressure suppression of superconductivity) for HoFeAsO$_{1-x}$F$_x$.

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